B 604,940

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

B 604,940

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

This set of
The Collected Works
of
Irving Langmuir
presented to

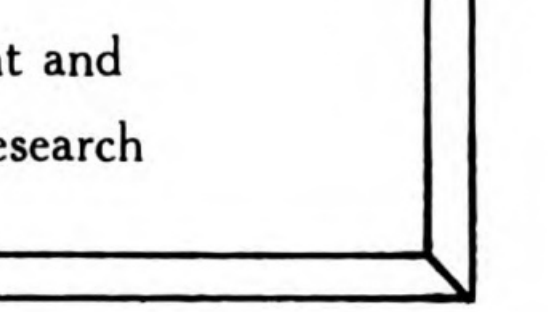
Dr. Michael Ference, Jr.

with the compliments of
GENERAL ELECTRIC COMPANY

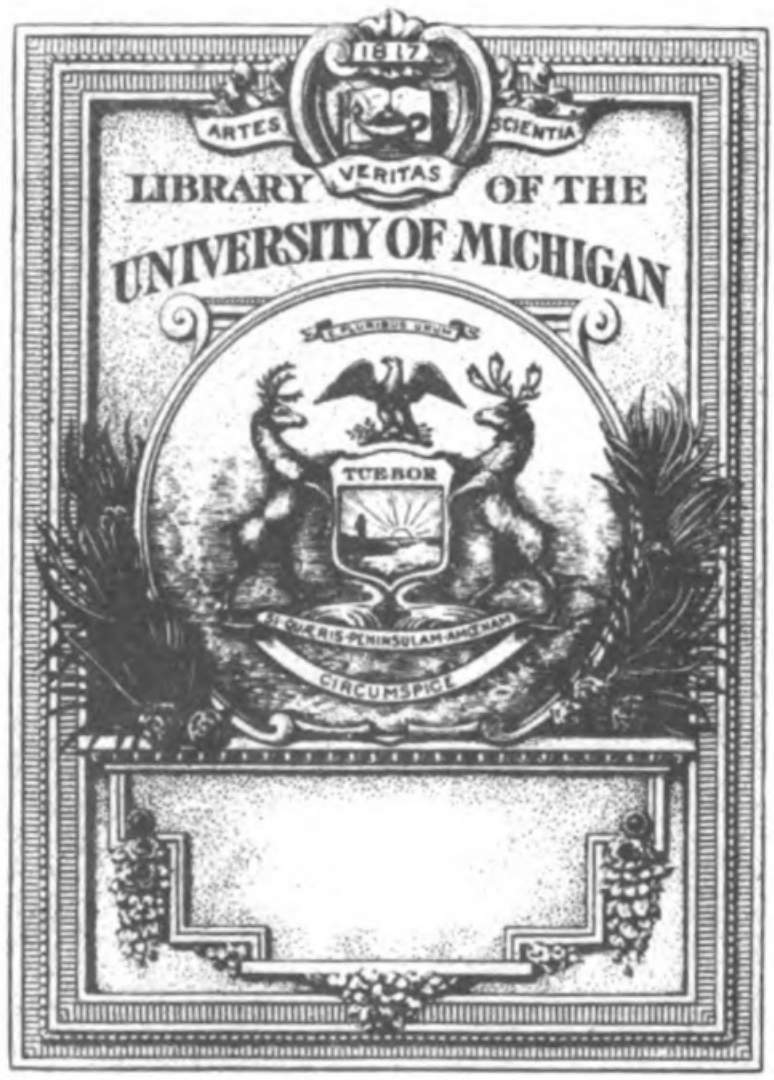
C. G. Suits

Vice President and
Director of Research

Digitized by Google



Original from
UNIVERSITY OF MICHIGAN



THE GIFT OF
Dr. Michael Ference

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE COLLECTED WORKS OF IRVING LANGMUIR

VOLUME 8

PROPERTIES OF MATTER

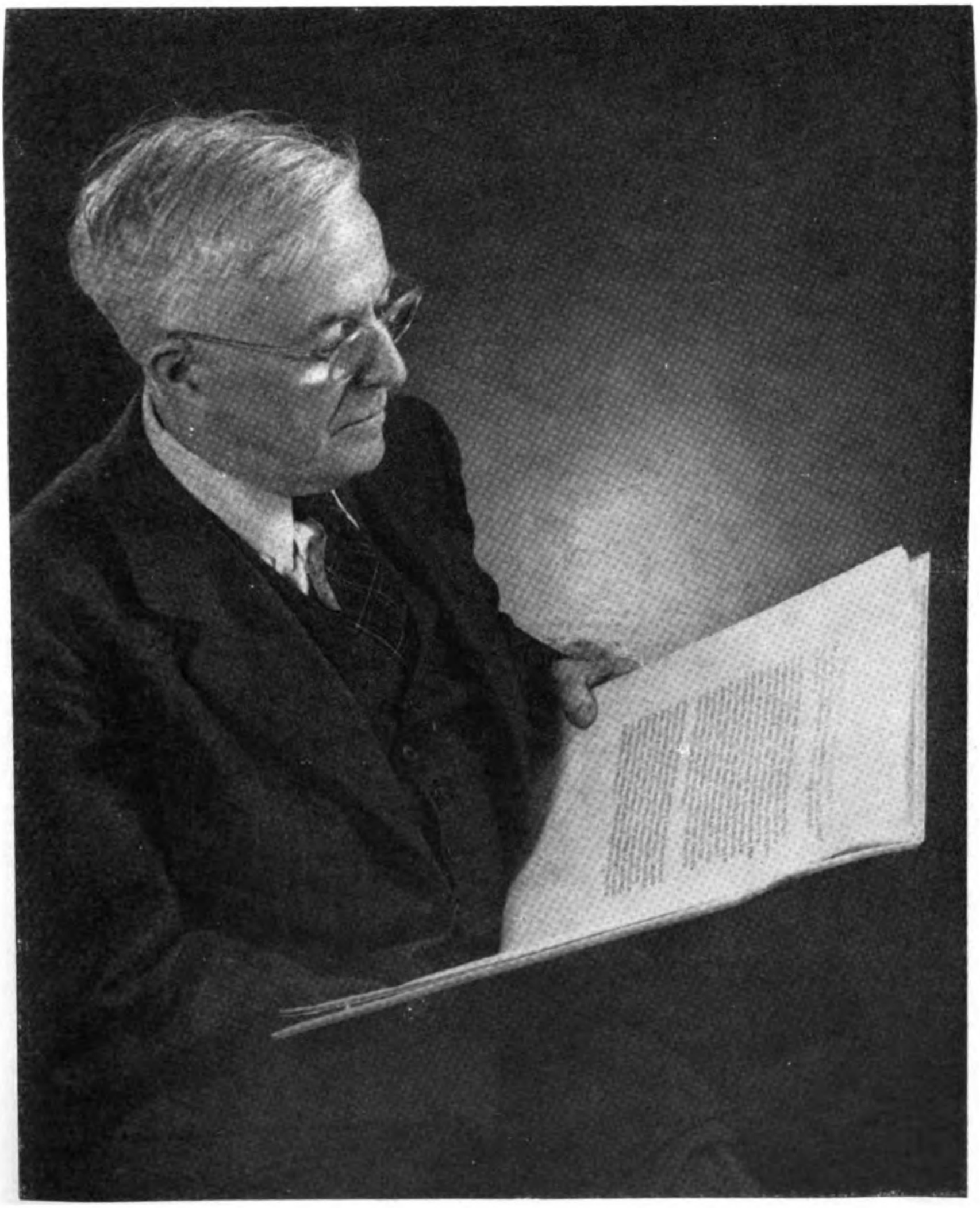
With a Contribution in Memoriam
by
DEAN HENRY EYRING

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN



Irving Langmuir — Research Scientist
General Electric Research Laboratory — 1909–1957
Nobel Prize Winner–1932

Digitized by Google
Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE COLLECTED WORKS OF
IRVING LANGMUIR

WITH CONTRIBUTIONS IN MEMORIAM
INCLUDING
A COMPLETE BIBLIOGRAPHY OF HIS WORKS

General Editor

C. GUY SUITS

VICE-PRESIDENT AND DIRECTOR OF RESEARCH
GENERAL ELECTRIC COMPANY

Executive Editor

HAROLD E. WAY

CHAIRMAN, DEPARTMENT OF PHYSICS
UNION COLLEGE
SCHENECTADY, N.Y.

Volume 8

PROPERTIES OF MATTER

Published with the editorial assistance of the General Electric Co. by

PERGAMON PRESS

NEW YORK · OXFORD · LONDON · PARIS

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Chemistry

Q
113
.L37

v 5

PERGAMON PRESS INC.,
122 East 55th Street, New York 22, N.Y.
Statler Center 640, 900 Wilshire Blvd.,
Los Angeles 17, Calif.

PERGAMON PRESS LTD.,
4 & 5, Fitzroy Square, London, W.1.
Headington Hill Hall, Oxford

PERGAMON PRESS S.A.R.L.,
24, Rue des Écoles, Paris V^e^, France

PERGAMON PRESS G.m.b.H.
Kaiserstrasse 75, Frankfurt am Main, Germany

Copyright for this compilation
©
1961
Pergamon Press Ltd.

Library of Congress Card No. 60-7068

Printed in Poland to the order of Państwowe Wydawnictwo Naukowe,
by Drukarnia im. Rewolucji Październikowej, Warsaw

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Chem
Gift
E. Michael Pavelec
9-11-75
1131572-110

HONORARY EDITORIAL ADVISORY BOARD

Chairman: Dr. C. GUY SUITS, General Electric Research Laboratory, Schenectady, N.Y.

Deputy Chairmen: Prof. P. W. BRIDGMAN, Harvard University, Cambridge, Mass.
Sir ERIC RIDEAL, Imperial College, London, England

Members: Prof. N. K. ADAM, Southampton University, Southampton, England
Prof. D. ALPERT, University of Illinois, Urbana, Ill.
Dr. L. APKER, General Electric Research Laboratory, Schenectady, N.Y.
Prof. J. BARDEEN, University of Illinois, Urbana, Ill.
Dr. J. A. BECKER, Bell Telephone Laboratories, Murray Hill, N.J.
Dr. K. B. BLODGETT, General Electric Research Laboratory, Schenectady, N.Y.
Dr. NIELS BOHR, Copenhagen, Denmark
E. G. BOWEN, CSIRO, Melbourne, Australia
Sir LAWRENCE BRAGG, Royal Institution, London, England
Dr. W. H. BRATTAIN, Bell Telephone Laboratories, Murray Hill, N.J.
Prof. P. W. BRIDGMAN, Harvard University, Cambridge, Mass.
Dr. H. R. BYERS, University of Chicago, Chicago, Ill.
Prof. A. H. COMPTON, Washington University, St. Louis, Mo.
Dr. W. D. COOLIDGE, General Electric Research Laboratory, Schenectady, N.Y
Prof. PETER DEBYE, Cornell University, Ithaca, N.Y.
Dr. B. DERJAGUIN, Institute of Physical Chemistry, Moscow, USSR
Dr. L. A. DUBRIDGE, President, California Institute of Technology Pasadena, Cal.
Dr. E. R. G. ECKERT, University of Minnesota, Minneapolis, Minn.
Dr. HENRY EYRING, University of Utah, Salt Lake City, Utah
Dr. DAVID HARKER, Roswell Park Memorial Institute, Buffalo, N.Y.
Dean J. H. HILDEBRAND, University of California, Berkeley, Cal.
Dr. A. W. HULL, General Electric Research Laboratory, Schenectady, N.Y.
Sir WILLIS JACKSON, Metropolitan-Vickers, Trafford Park, England
Dr. ZAY JEFFRIES, Vice-President, General Electric Co. — *retired*. Pittsfield, Mass.
Prof. A. F. JOFFE, USSR Academy of Sciences, Moscow, USSR — *deceased*
Dr. K. H. KINGDON, General Electric Research Laboratory, Schenectady, N.Y.
Prof. V. K. LAMER, Columbia University, New York City, N.Y.
Dr. D. A. MACINNES, Rockefeller Institute, New York City, N.Y.
Dr. C. E. K. MEES, Honolulu, Hawaii
Dr. V. J. SCHAEFER, Munitalp Foundation, Schenectady, N.Y.
Prof. N. N. SEMENOV, Institute of Chemical Physics, Moscow, USSR
Dr. HARRY SOBOTKA, Mount Sinai Hospital, New York City, N.Y.
Dr. L. TONKS, General Electric, Pleasanton, Cal.
Dr. A. VON ENGEL, Oxford University, Oxford, England
Dr. WARREN WEAVER, Rockefeller Foundation, New York City, N.Y.
Dr. E. J. WORKMAN, President, New Mexico Institute of Mining and Technology, Socorro, N.M.

Executive Editor: Dr. HAROLD E. WAY, Union College, Schenectady, N.Y.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

FOREWORD

THE PLAN to publish a memorial to Irving Langmuir, including all of the scientific output of his brilliant career in research, was announced to me by Captain I. R. Maxwell, managing director of Pergamon Press, late in 1958. My associates and I were asked to aid the venture by providing editorial advice and counsel, by enlisting the cooperation of scientific friends and acquaintances, and by assisting in the collection and identification of material. Our enthusiasm for the project and our willingness to cooperate sprang from two important considerations.

First, Langmuir's career provides an outstanding example of how free, but discriminating, inquiry in pure science may yield not only vital new knowledge and understanding of nature, but also a great bounty of practical usefulness for society. Secondly, Langmuir's associates hold him not only in great respect, but in very great affection as well. Hence the preparation of these volumes has been more than a service; it has been a labor of love.

The original plan was to publish Langmuir's works in three or four volumes, but for very good reasons, which developed during the course of the project, the series has grown to twelve volumes. The quantity of Langmuir's published scientific work proved to be far greater than we had estimated, and some previously unpublished wartime research and reports on meteorological studies were of such importance that their inclusion in the volumes was mandatory. Moreover, some exceptionally interesting philosophical papers and publications served to round out the literary portrait of Langmuir as a man and as a scientist.

My associate editors, Sir Eric Rideal and Professor P. W. Bridgman, have contributed generously from their great wealth of knowledge and their intimate acquaintance with Dr. Langmuir. It is a pleasant duty to acknowledge that the many members of the Honorary Editorial Advisory Board have participated in this venture with enthusiasm, and that their editorial contributions to the separate volumes have added tremendously to the appraisal and interpretation of Langmuir's collected works. I particularly want to acknowledge with gratitude the valuable work of Professor Harold E. Way of Union College who, in the capacity of Executive Editor, has carried the major task of assuring that our responsibilities and commitments were fulfilled.

I first met Irving Langmuir in the General Electric Research Laboratory when I joined the research staff in 1930, but our first meeting might equally well have taken place on a ski hill in the Adirondacks, at Lake George where

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

he liked to spend the summer, or on a climb on Mt. Marcy, for he had a prevailing love of the out-of-doors. Whether in the Laboratory or in the mountains, an intense curiosity about natural phenomena constantly pervaded his thoughts. In fact, I have never met anyone else who was *so well coupled to nature*.

I am sure that, like all observant people, Langmuir perceived the beauty of nature as portrayed by the qualities of form, color, mass, movement, and perspective. In addition, however, Langmuir was delighted and entranced even more by the challenge to understand the working of nature as portrayed in the phenomena of everyday life — clouds, ripples on water, bubbles in ice, the temperature fluctuations of air and of water, the plastic quality of snow, the flight of a deer fly, and the thousands of "simple" phenomena which nearly everyone takes for granted. These manifestations of nature held endless fascination for Langmuir, and he constantly challenged himself to explain basic phenomena in terms of known laws of science. Of course, the same curiosity characterized his work in the Laboratory, and hence, provided the unifying motivation for his career, whether at "work" or at "play".

Langmuir's scientific work is so completely and perceptively described and appraised in the separate volumes of this work that only a few general comments and observations are appropriate, or indeed possible, at this point.

One striking feature of his research method was its instrumental simplicity. Although his career extended into the glamour age of science, characterized by large, impressive, and expensive machinery such as the cyclotron, the synchrotron, and particle and radiation diffraction equipment, his own experiments were almost invariably simple and uncluttered. He seemed positively attracted to simple experimental techniques, in refreshing contrast to what sometimes appears to be a fashionable reliance on impressive and expensive complexity of research equipment. His work with heat transfer in gases, and later with electron emission phenomena from metals, employed laboratory glassware of stark simplicity. His studies of surface films, especially films on water, employed beautifully simple experimental equipment. The Laboratory work on aerosols and smokes, and later on the nucleation of supercooled clouds, was all carried on with apparatus that could be assembled from the equipment of a typical home. His classical experiments on the "speed of deer fly" came about as close as possible to the string, wax, and paperclip approach to science; yet they sufficed to establish the essential facts sought by the investigation. Probably few scientists, before or since Langmuir, have gained so much important new knowledge of nature with such simple research equipment.

Similarly, Langmuir preferred to work with a few collaborators, rather than a large group or team of researchers, for this favoured a close contact with the work on a participating basis. His ability to apply mathematical analysis to physical problems was of a high order, and he divided his time about equally between experimental work and theoretical work. The combination

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of outstanding experimental and analytical ability which he possessed occurs but rarely in a single individual; most scientists have somewhat greater interests, aptitudes, and hence accomplishment in one area or the other.

Langmuir almost invariably worked on an intense basis and was generally completely preoccupied with his current problems. His concentration was exceptional, and he might pass you in the hall without seeing you. If you reminded him of it, he would smile and acknowledge that he was highly excited about some experiments that were in progress, or about some calculation that was presenting some puzzling aspects.

We spend a good deal of time and thought nowadays on the question of motivation for scientists, seeking to understand the source and character of their drive. In Langmuir's case, one needs to inquire no further than his curiosity. This pronounced trait provided an intense internal source of motivation, which constantly drove him to inquire and probe and test hypotheses until a pattern of understanding was developed. When he was on the trail of an exciting mystery, which was usually the case, his intense concentration was remarkable to behold.

Langmuir's career contributes much to our understanding of creative output in research. For example, on the perennial question of creativity and age, it has been held by some that the bulk of human creative work is accomplished in early adult life, say in the age bracket between 25 and 35 years. It is probable that some purely statistical information might support this view. However, I would disagree strongly with the corollary conclusion that creative ability is characteristic of this age bracket. In the Laboratory, it is not unusual for creative young workers to acquire a greater span of research guidance, counselling, and even management responsibility as their career matures, and hence their creative contribution will, to a corresponding degree, appear in the work of others. I believe that in such cases scientists are generally not less, but more creative with advancing age, frequently up to and even through retirement. It is clear that purely statistical information would not readily reveal this fact.

It is interesting to examine Langmuir's career as an example of a scientist who remained in active research up to and through retirement, to see what role age played in his output. In Volume 12 we have depicted Langmuir's achievements as a function of his age, using his scientific *publications* as evidence of his gross scientific output, and his *principal accomplishments* as evidence of his creative output. The resultant charts show remarkably constant productivity throughout his scientific career, and even through retirement. Throughout this period Langmuir published an average of five to six scientific papers per year. His principal accomplishments, both scientific and practical, took place almost uniformly over the period of his researches. Certainly no "creative age" can be identified in his career. The example of Langmuir's scientific history does not prove the general thesis, but from the observation

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of many research careers, I am persuaded that human creativity in science is not a significant function of age.

Creative output, however, *is* a function of many other factors that comprise the research environment. One important factor is the changing field of research. Some of the most creative scientists in the history of the General Electric Research Laboratory have worked intensively in one field for a period of some years, and have then changed quite abruptly to a new field as a source of fresh stimulation and new challenge. It is evident that in a period of 5 years, or so, one can bring a fresh point of view to a new field, make a major contribution and perhaps exhaust one's ideas on the subject. At that point of fruition, there is a great temptation to sit back and bask in a reputation for eminence which has been established in a specialized field of science. The more courageous scientist, however, will be challenged, or will, like Langmuir, challenge himself to enter a new field. This requires courage, because in the new field he will be a neophyte but, at the same time, a scientific entrepreneur with a reputation at risk, and this risk may not pay off.

Langmuir's career exemplifies the courageous entrepreneur in science. It would be difficult to find a common demoninator, except curiosity, in many of the fields of science in which he made basic contributions. He never hesitated to attack new fields, such as protein monolayers, the generation of smoke, or meteorology, which were completely new and, hence, challenging territory to him. In each of these diverse fields, and in a great many others, he has made major basic contributions.

Some discussion of the very important applied aspects of Langmuir's scientific work is appropriate. It is a fact that, although his prevailing motivation in research was curiosity about all natural phenomena, he was always perceptive of the practical usefulness of research results, and he himself suggested possible practical applications of many of the new phenomena which he discovered. He was generally able to communicate his enthusiasm to applied scientists and engineers interested in the proposed application and to give them guidance in its exploration.

It is interesting to speculate on the way that Langmuir's career might have developed had he chosen an academic, rather than an industrial environment for his work in science. My personal belief is that his research would, in any environment, have resulted in a high order of scientific accomplishment. Although he evidenced little interest in teaching, he was in fact an outstanding teacher, and in a university he would have exerted a great influence on students who might have been fortunate enough to be in contact with him. But I doubt if an academic career for Langmuir would have, or could have, developed the great bounty of useful results for society which did come from his exposure to a creative industrial scientific environment. The human and economic impact of gas-filled lamps, high-vacuum electron tubes, atomic-hydrogen welding, space charge emission phenomena, techniques and discoveries in

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

surface chemistry, thyratron arcs (with A. W. Hull), and cloud seeding techniques has been very great indeed, and in most of these developments the influence of his research environment has been unmistakable.

Wherever Langmuir worked, or might have worked, the world is vastly better because of him, and both his former associates and colleagues, and the public at large, bear a tremendous debt of gratitude for his genius in science and for his perception of human need.

June 15, 1960

C. GUY SUITS
Vice-President and Director of Research
General Electric Company
Schenectady, New York

Digitized by Google
Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

PREFACE TO VOLUME 8

THE FIRST part in this volume contains only two papers, both dealing with "The Constitution and Fundamental Properties of Solids and Liquids". These two papers were published in 1916 and 1917 before the advent of quantum mechanics and, at the time of their publication, represented definitive work in the field. Their importance can scarcely be exaggerated. The first paper reviews in detail the theories of Werner, Stark, J. J. Thompson, and Lewis on chemical constitution. It contains a critical study of the phenomena of condensation and evaporation of solids. The second paper deals more with the structure of liquids and the relationship between liquids and solids, with considerable emphasis on surface tension.

The second part is again concerned with surface chemistry but has to do with specific phases instead of the wide coverage noted in the first part. Included in this volume is the Nobel Laureate Lecture Langmuir delivered in Stockholm in 1932.

Dr. Henry Eyring, Dean of the Graduate School, University of Utah, long-time personal friend of Langmuir and an eminent physical chemist, was invited to write the contributed article for this volume.

HAROLD E. WAY
Executive Editor

Digitized by Google
Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

CONTENTS

	Page
FOREWORD BY DR. C. GUY SUITS, *General Editor*	vii
PREFACE BY DR. HAROLD E. WAY, *Executive Editor*	xiii
PART 1. FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS	
INTRODUCTION TO VOLUME 8 BY DEAN HENRY EYRING	xvii
THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. I. SOLIDS	1
THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. II. LIQUIDS	73
PART 2. INTERFACIAL PHENOMENA	
THE CONSTITUTION OF LIQUIDS WITH ESPECIAL REFERENCE TO SURFACE TENSION PHENOMENA	133
THE SHAPES OF GROUP MOLECULES FORMING THE SURFACES OF LIQUIDS	137
THE MECHANISM OF THE SURFACE PHENOMENA OF FLOTATION	144
SURFACE CHEMISTRY. NOBEL LECTURE	158
SURFACE CHEMISTRY. THE DENKI-GAKKWAI	191
TWO-DIMENSIONAL GASES, LIQUIDS AND SOLIDS	217
SURFACE ELECTRIFICATION DUE TO THE RECESSION OF AQUEOUS SOLUTIONS FROM HYDROPHOBIC SURFACES	225
REPULSIVE FORCES BETWEEN CHARGED SURFACES IN WATER AND THE CAUSE OF THE JONES-RAY EFFECT	232
APPENDIX I	337
APPENDIX II	239

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

INTRODUCTION TO VOLUME 8

A CONTRIBUTION IN MEMORIAM

BY DEAN HENRY EYRING

Valence and Van der Waals Attraction

LANGMUIR in 1916 and 1917 was deeply involved in consideration of the forces holding atoms and molecules together. It would be difficult to suggest a better method for sensing the perplexities of pre-quantum mechanical bonding theory than to study Langmuir's papers, particularly those in Part 1. Here Werner's coordination bond theory and Stark's electron pair bond model are both discussed. Stark's picture was not unlike the Bohr model of H_2 in which two Bohr atoms share the pair of electrons equally and as a result of this sharing are bound together. J. J. Thomson's concepts were similar to Stark's. In Thomson's electron affinity model he visualized the binding together of atoms in polar bonds in a molecule such as water as due to charge transfer much as we do today. The homopolar bond gave him more trouble. He supposed uncharged atoms were held together by one or more doublets located in the atoms. Thomson's theory lacked the idea of saturation of valence exemplified in the homopolar bond. He expected three hydrogen atoms to form rings with each atom bonding with both neighbors and he saw no reason why carbon might not form eight bonds. Langmuir was too familiar with chemistry to be happy about such exotic valences.

It remained for G. N. Lewis[1] in his 1916 paper to distinguish sharply between homopolar and polar bonds and to emphasize the importance of the electron pair bond. Kossel[2] at about the same time emphasized the importance of closed shells of eight as in the rare gases and in various anions. The Lewis theory provided a point of departure for later important valence considerations of Langmuir. In the papers of Part 1, Langmuir was concerned with primary valence and the "secondary valences" which held saturated molecules together in crystals and liquids. Accounting for the latter was a real problem.

These papers help us to see that quantum mechanics wasn't required to discover the benzene ring nor the tetrahedral carbon atom in the aliphatic hydrocarbons although it did help in the quantitative understanding of these structures. What wave mechanics did do was to provide a picture of electrons as standing waves situated at least part of the time in the space between the atoms bound together. The Pauli principle replaced the fiction of attraction

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

between the electrons of an electron pair bond with the concept that two electrons providing they have unlike spins can jointly occupy and saturate a bond orbital. That there was no satisfactory explanation of the valence bond in 1917 is shown by the following quotation from Langmuir's paper "The Constitution and Fundamental Properties of Solids and Liquids, II. Liquids."

> "Nothing definite is known regarding the forces acting on electrons inside atoms. There seems to be increasing evidence that the electrons in atoms are not revolving in orbits around the positive nuclei, but should rather be regarded as stationary except when disturbed from their equilibrium positions by exeternal forces. It may be, however, that a magnetic field (Parson's theory) is to be associated even with stationary electrons in the atom. If this viewpoint is correct, we can no longer fall back on the convenient centrifugal force to explain why the electrons do not fall into the positive nucleus."

Langmuir's continuation of this discussion is likewise of historic interest.

London's quantum mechanical explanation of Van der Waals forces answered the puzzle as to the forces causing gases to condense. These "secondary valences" are due to the oscillating electric dipoles formed by electrons vibrating about nuclei in phase with the electric dipoles in neighboring molecules.

These early papers delineate with clarity the origins of theories of valence.

The Langmuir Adsorption Isotherm and Surface Films

Langmuir's work on adsorption has tremendously influenced the subsequent development in the field of surfaces. His spreading film experiments gave us a clear picture of films as monolayers oriented with respect to the surface with measurable cross sections that check with later X-ray measurements. In his paper 185, Langmuir explains the Jones-Ray effect. An electrolyte lying between two parallel plates of like charge exerts a repulsive force which is measurable when one plate is the glass wall and the other is the liquid surface. The effect is to bind a film of liquid to the inside of a tube and so give it effectively a smaller diameter with a resultant greater capillary rise of a liquid column. This apparent increase in surface tension is the Jones-Ray effect and the theory of it is clearly developed by Langmuir.

His experiments on spreading of monofilms on liquid surfaces as well as the adsorption of single layers of gases on solid surfaces showed that the model of Laplace and other theorists who assumed fields of force extending over many layers must be replaced by a model in which the short range forces extend very little beyond the adjacent layer. Thus the transition from vapor to liquid probably takes place essentially in a few surface layers. The surface is, however, far from smooth especially as critical conditions are approached.

Van't Hoff assumed that at equilibrium the forward reaction was just balanced by the backward reaction and Langmuir used this to derive his

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

famous adsorption isotherm. Wallenstein and the writer[3] used this reaction rate procedure to derive various kinds of statistics. The procedure is outlined in a section of one of their papers which we quote here.

"For generality we shall refer to a number, n, of units which may, in various particular cases, be atoms, molecules or elementary particles and a number of sites which may be adsorption sites on a surface, or a set of quantum states, also depending on the phenomenon under consideration. Let the number of these sites be ω_i and the energy of interaction between any one of these sites and a unit be E_i. This quantity in the ideal case will be constant for all sites being considered, but in other cases, it may vary from one site to another. This will not affect the general theory but, in application, will necessitate a knowledge of E_i as a function of coverage. We shall consider the instant when n_i units are adsorbed on the ω_i sites leaving n_g free units in some volume V. This volume will for the present be considered large enough so that the free units possess the properties of an ideal gas. At any instant the n_i adsorbed units are leaving the sites at a velocity $n_i k'_i$ where k'_i is the specific rate constant for the dissociation of a site and an absorbed unit. The reverse process in which free units go over to the bound state requires some consideration. If the process is one of saturation, then clearly, the instantaneous number of unsaturated sites is $(\omega_i - n_i)$ and the rate at which units disappear from the free state is $k'_g n_g(\omega_i - n_i)$, where again k'_g is the specific rate constant. At equilibrium the two rates are equal; hence

$$k'_i n_i = (\omega_i - n_i) n_g k'_g \tag{1}$$

This is the general equation for any phenomenon involving saturation.

"For the case where a site can accommodate an unlimited number of units, the expression corresponding to (1) may be derived by appealing to the principle of detailed balance.[4] Whereas, in deriving equation (1), the situation could be pictured as in Fig. 1 in which a unit, O, completely saturates a site, X, the case here is as indicated in Fig. 2. As before, any one of the n_i units is a candidate for removal to the free state. If at any time a unit such as O in Fig. 2, leaves its bound position, then according to the principle of detailed balance there must be a reverse process which replaces this unit. Thus, in effect, the crosses in Fig. 2 indicate possible sites for accommodation of a gas molecule so that, at any instant, the number of effective sites for the accommodation of a free unit is $(\omega_i + n_i)$ and at equilibrium

$$k'_i n_i = (\omega_i + n_i) n_g k'_g \tag{2}$$

"Equation (2) can be considered as the general equation for any process in which a given site can accommodate an unlimited number of units. It will be referred to as the general equation of condensation statistics.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

FIG. 1.

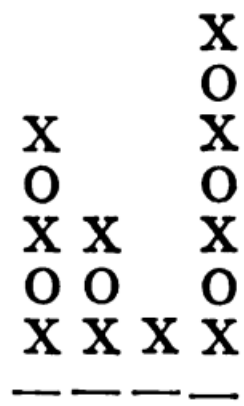


FIG. 2.

"In either the case of saturation or condensation statistics it may be that for a given situation $n_i < \omega_i$ at equilibrium, so that both (1) and (2) reduce to

$$k_i' n_i = \omega_i n_g k_g' \tag{3}$$

Such a relation obviously corresponds to the reduction of quantum statistics to classical statistics. This form is also obtained if we consider the case illustrated by

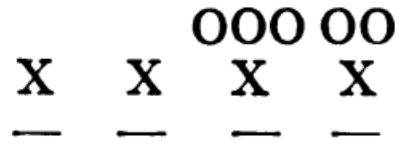


FIG. 3.

Fig. 3 in which a unit interacting with a site neither uses up the site nor creates a new one as in the previous cases.

"Let us next consider the case where a site is saturated by d units. Then in place of equation (2), we have

$$k_i' n_i = (\omega_i + n_i) n_g k_g' - p(d+1)\omega_i n_g k_g' \tag{4}$$

where p is the probability that any one of the ω_i sites has become saturated and thus deletes $(d+1)$ condensation sites from the set $(\omega_i + n_i)$. In the special case in which d is infinite, p reduces to zero whence equation (4) reduces to (2). When d is unity the $p = n_i/\omega_i$ and equation (4) reduces to equation (1), as it must. Thus, equation (4) is the general result for all types of condensation but the values of p are not of such simple form for other values of d. Equation (4), with a suitable expression for p, is appropriate, for example, for treating condensation in a capillary d units in width. Gentile[5] has treated certain aspects of this problem.

Applications

"Let us now consider equations (1) and (2) together in the form

$$k_i' n_i = (\omega_i \pm n_i) n_g k_g' \tag{5}$$

According to absolute reaction rate theory, the specific rate of any unit process can be written

$$k' = \frac{\Sigma_i e^{-\epsilon_i/kT} \nu_i \gamma_i + \varkappa' \dfrac{kT}{h} F^{\neq} e^{-\epsilon^{\neq}/kT}}{F} \tag{6a}$$

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Here F is the partition function for molecules of the reacting species entering into the activated complex and $F^{\neq}$ that for the activated complex. $\varepsilon^{\neq}$ is the energy of activation at absolute zero. The first term in the numerator of (6) takes care of the possibility of leakage through the potential barrier between reactants and products. In this term, ε_i is the energy of the system in the ith state ($\varepsilon_i < \varepsilon^{\neq}$), ν_i is the frequency of vibration in the ith state and γ_i is the chance per vibration of passing from the initial to the activated state. $\varkappa'$ is the transmission coefficient for complexes with energies as large or larger than $\varepsilon^{\neq}$. Under most circumstances, we simply write

$$k' = \varkappa \frac{kT}{h} \frac{F^{\neq}}{F} e^{-\varepsilon^{\neq}/kT} \tag{6b}$$

which defines $\varkappa$, the complete transmission coefficient. For many systems of interest $\varkappa$ can be taken as unity. Substituting (6) in (5) and cancelling similar terms on either side yields

$$\frac{n_i}{F_{gs}} e^{-\varepsilon^{\neq}_{gs}(i)/kT} = \frac{(\omega_i \pm n_i) n_g}{F_g F_s} e^{-\varepsilon^{\neq}_{g}+s(i)/kT} \tag{7}$$

The subscripts g and s refer to the free units and sites, respectively, and gs refers to the combined unit and side in the complex or the products. Writing $\varepsilon_i = \varepsilon^{\neq}_{gs}(i) - \varepsilon^{\pm}_{gs(i)}$, which is just the energy of the process represented by (5) at absolute zero, and solving for n_i yields

$$n_i = \frac{\omega_i}{\frac{F_g F_s}{F_{gs} n_g} e^{\varepsilon i/kT} \pm 1} \tag{8}$$

Under the assumption that the free units have the properties of an ideal gas, the partition function per molecule is

$$F_g = \frac{(2\pi m k T)^{3/2}}{h^3} V j^{(T)} \tag{9}$$

where $j^{(T)}$ represents the internal degree of freedom of the free units. The free energy of the n_g free units in the volume V is then

$$F = n_g kT \ln \frac{(2\pi m k T)^{3/2}}{h^3} \frac{V}{n_g} j^{(T)} \tag{10}$$

$$= -n_g kT \ln \frac{F_g}{n_g} \tag{11}$$

The chemical potential, μ, per molecule then satisfies the equation

$$\frac{\mu}{kT} = -\ln \frac{F_g}{n_g} \quad \text{and} \quad \frac{F_g}{n_g} = e^{-\mu/kT} \tag{12}$$

Digitized by Google Original from UNIVERSITY OF MICHIGAN

This result in (8) gives

$$n_i = \frac{\omega_i}{\frac{F_s}{F_{gs}} e^{(\epsilon_i - \mu)/kT} \pm 1} \tag{13}$$

"From this equation, we may begin to consider special cases. For electrons, it is clear that F_s and F_{gs} are both unity so that

$$n_i = \frac{\omega_i}{e^{(\epsilon_i - \mu)/kT} + 1} \tag{14}$$

This is just the equation of Fermi-Dirac statistics. Similarly, for any particles of even parity, we have, for the same reasons, the equation for Bose-Einstein statistics:

$$n_i = \frac{\omega_i}{e^{-(\epsilon_i - \mu)/kT} - 1} \tag{15}$$

Frenkel[6] has used a kinetic approach to derive Bose-Einstein and Fermi-Dirac statistics."[7]

Further development of this reaction rate point of view is to be found in our quoted paper and in a treatment of capillary adsorption Landsberg[8] has extended this procedure and related it to a statistical approach by Brilluoin.[9] It is interesting that Langmuir's adsorption isotherm and Fermi-Dirac statistics are the same statistics. I shall now outline certain of our developments of liquid and surface theory which supplement Langmuir's considerations.

The Method of Significant Structures

For condensed systems of the kind considered by Langmuir one needs appropriate partition functions if equilibrium and rate processes are to be treated expeditiously. Gases or liquids in bulk or as films offer no particular problem since partition functions for gases and for Einstein and Debye solids are well understood. A satisfactory liquid partition function, however, has not been available and our current efforts to rectify this situation will be summarized briefly.

As was noted earlier[14] the specific heat of argon at constant volume, C_v, is very well represented by the equation

$$C_v = \frac{V_s}{V} 6 + \frac{V - V_s}{V} 3$$

Here V_s and V are the molal volume of solid and liquid respectively. This suggests that a particular degree of freedom in a liquid spends the fraction V_s/V of its time in a solid-like state and the rest of its time $V - V_s/V$ in a gas-like state. The well known absence of suitable nuclei for either freezing or boiling in pure liquids shows that there is nothing like a solid or liquid phase

Digitized by Google Original from UNIVERSITY OF MICHIGAN

but only intimate admixtures of these two types of degrees of freedom with rapid transformation back and forth as indicated by the fluidity. The chance of one molecule being in collision with some one of the other molecules must be close to V_s/V. Also our assumption leads to the Van der Waals' dependence of the energy on volume. Thus for the partition function, f, of a mole of liquid we write

$$f = (f_s)^{\frac{V_{sN}}{V}} (f_g)^{\frac{V-V_{sN}}{V}} \tag{1}$$

The twelve per cent expansion that occurs upon melting of argon, with similar percentages for other normal liquids, along with the X-ray evidence that the nearest distance between pairs is about the same in liquids and solids suggests that much of the expansion is due to stacking faults and other types of imperfection found also in imperfect solids. In close packed systems a common stacking fault occurs where cubic and hexagonal close packed structures are in contact. Along this line of contact alternate equilibrium positions are provided for molecules at an added volume of only a fraction of a molecular volume. However, of all the positions open to a particular molecule only one will be freely accessible. The others require a strain energy, a'/n_h where a' is a constant. The number of holes, n_h, has the value $n_h = n[(V-V_s)/V_s]$. Here n is the number of additional equilibrium positions a molecule acquires when the extra volume $V-V_s$ equals the solid volume V_s. The liquid partition function thus becomes

$$f = \left\{ \frac{e^{\frac{E_s}{RT}}}{\left(1-e-\frac{\Theta}{T}\right)^3} \left(1+n\,\frac{(V-V_s)}{V_s}\,e^{-\frac{aE_sV_s}{(V-V_s)RT}}\right) \right\}^{N\frac{V_s}{V}} \left\{ \left(\frac{(2\pi mkT)^{3/2}}{h^3}\,\frac{eV}{N} \right)^{N\frac{V-V_s}{V}} \right\} \tag{2}$$

The last bracket comes from the assumption that gas-like molecules are free to share communally the extra volume $(V-V_s)$. Thus the volume factor in the gas partition function $(V-V_s)^{N[(V-V_s)/V]}$ is divided by

$$\left(N\frac{(V-V_s)}{V}\right)! \simeq \left(\frac{N(V-V_s)}{eV}\right)^{\frac{N(V-V_s)}{V}}$$

giving

$$\left(\frac{eV}{N}\right)^{\frac{N(V-V_s)}{V}}$$

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The first bracket above is the expression for the Einstein solid multiplied by the extra factor

$$\left(1+n\frac{V-V_S}{V}e^{\frac{aE_sV_s}{(V-V_s)RT}}\right)$$

This factor arises from the degeneracy due to the extra equilibrium positions.

Now for argon Fuller, Ree and Eyring[10] use the solid parameters $E_S = 1888.6$ calories, $V_S = 24.98$ c.c. and $\theta = 60$. Choosing $n = 10.8$ and $a = .00534$ they obtain the following calculated values which are compared with the observed values.

TABLE I

	V_m c.c.	S_m e.u.	P_m atms	V_b c.c.	S_b e.u.	T_b °K
Calculated	28.90	3.263	.732	29.33	19.04	87.29
Observed	28.03	3.35	.674	28.69	17.85	87.29
Per cent error	+3.11	−2.61	+8.55	+2.22	+6.68	0

Here the subscripts m and b label melting and boiling temperature properties respectively. For the critical properties of argon they find:

TABLE II

	Calc.	Obs.	Δ%
T_c°K	149.7	150.66	−0.637
$V_c$ml	83.68	75.26	+11.2
$P_c$atm	52.93	48.00	+10.3

Similar agreement has been found for the other rare gases and for nitrogen, methane, benzene[11] and for chlorine[12] and for the metals[12a] and the molten salts.[13] It should be possible to treat concentrated strong electrolytes successfully as a combination of a "hydrated molten salt structure" together with the structure in which an ion is surrounded by the Debye-Huckel ionic atmospheres. The theoretical justification for writing the partition function as a product of terms representing the various sructures is that one chooses the largest product term of a series in which the other terms may be neglected. This is ordinarily a satisfactory procedure with grand partition functions. J. D. Bernal[15] has discussed the possible geometrical structures to be expected in a liquid that does not fill space and so are inconsistant with the long range order of the solid.

The method of significant structures is instructive in examining surface tension and the properties of surface films. A surface layer has a thickness

Digitized by Google Original from UNIVERSITY OF MICHIGAN

$(V/N)^{1/3}$ where V is its molal volume and N is Avogardo's number. One square centimeter of the transition layer contains then $(V/N)^{1/3}V^{-1}$ moles.

If we replace E_s in equation (2) by $E_s(1/2+1/4\ \varrho_e/\varrho+1/4\ \varrho_g/\varrho)$ we get the upper curve in Fig. 1 for the Helmholtz free energy as a function of volume for a mole of surface molecules at a temperature T. Here ϱ, ϱ_e, and ϱ_g are the density of the surface layer of liquid density and gas density respectively. The lower curve is the Helmholtz free energy plotted against volume for a mole of bulk liquid. The difference in Gibbs' free energy $(F'-F)$ between the intercepts on the axis of ordinates of the two tangents multiplied by $(V/N)^{1/3}/V$ the number of moles in a layer 1 sq. cm in area is then the contribution of the layer to the surface energy. To this must be added the free energy contributions of the second layer calculated analogously. The densities ϱ of the different layers must be made self consistant. Practically this is accomplished best by an iterative process. Actually ninety-five per cent of the contribution to the surface free energy comes from the top liquid layer with the rest from the second layer. Chang, Ree and the author will report extensive calculations in this field elsewhere. The surface energy of liquid neon is calculated within four per cent. Hill[16] has discussed the transition layers between phases and related his procedure to earlier theories in a very interesting way. Henniker[17] has discussed the surface zone of liquids and cited the evidence for orientation of layers far below the surface layer. The evidence cited does not seem sufficient to discard the concept of Langmuir and others that the free energy change is largely restricted to a single or a very few transitional layers. Adam's[18] discussion is interesting in this connection.

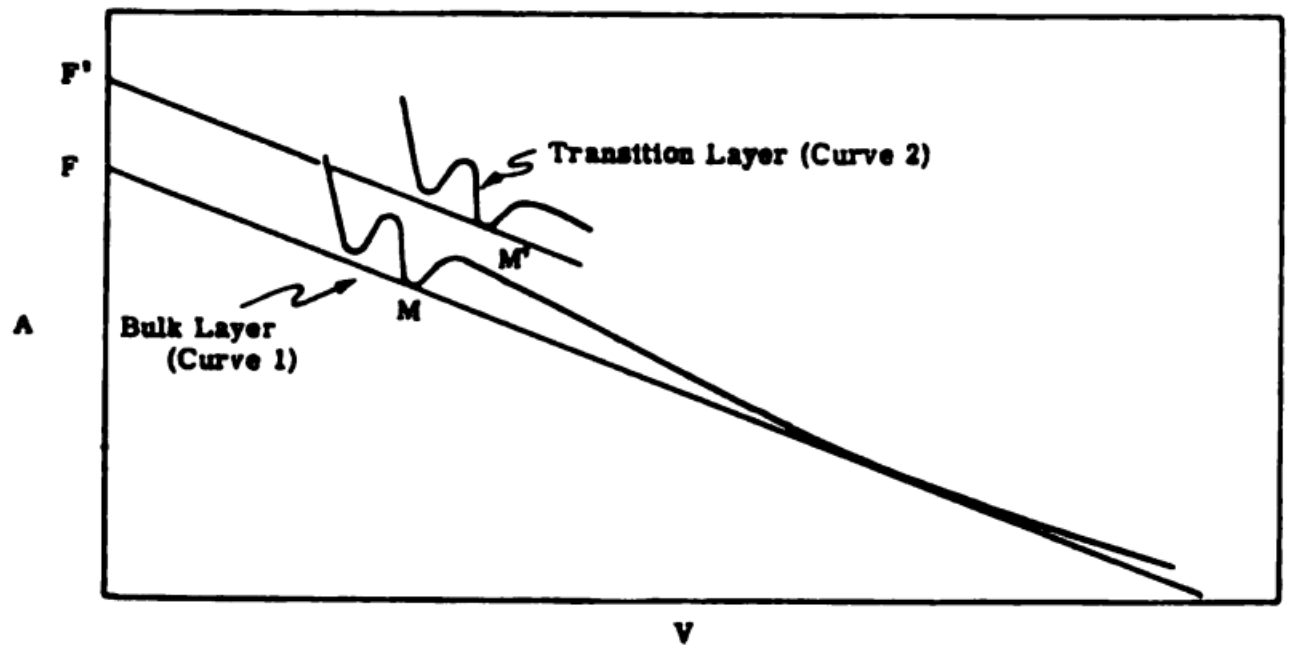


FIG. 1. A schematic diagram of bulk (Curve 1) and surface layer (Curve 2) Helmholtz free energies as a function of volume at temperature T. The pressure is given by the slope of the two tangents which are necessarily equal, and F' and F are the corresponding Gibbs free energies.

Fig. 1 allows us to see why pressure has only a small effect on surface tension. Thus increasing the pressure corresponds to making the two parallel tangent lines $F'M'$ and FM steeper but keeping them parallel. Such a pressure increase

Digitized by Google Original from UNIVERSITY OF MICHIGAN

can only change slightly the contribution to the surface free energy $(F'-F)/N^{1/3}V^{2/3}$ made by a transition layer, since there will ordinarily be only a small curvature difference at the minima between M' and M.

The effect of adding a solute which concentrates preferentially in the transition layer will lower curve 2 more than curve 1 in Fig. 1 and so decrease the surface energy in accord with the Gibbs adsorption isotherm. The converse is of course true if the solute concentrates in the surface layer. A solute with a lower critical temperature than the solvent should preferentially dissolve in the less dense surface layer and so lower the surface tension and conversely. Hildebrand and Scott's[19] book on solubility together with the theory presented here for the difference in nature between surface and bulk layers suggests a quantitative theory of solute effect on surface tension.

Condensation and Evaporation

Langmuir frequently made use of the equation $p/\sqrt{2\pi mkT}$ for the number of molecules colliding with a square centimeter of surface per second. This can only give the number of vapor molecules that condense per second per square centimeter of surface if every molecule sticks. If only the fraction $\varkappa$ of the molecules which collide stick we get for the condensation rate, $R = \varkappa p/\sqrt{2\pi mkT}$. The transmission coefficient, or condensation coefficient, $\varkappa$, is frequently less than unity. The reasons for this are instructive and are indicative of surface structure. It is observed that molecules without rotational degrees of freedom, or those which rotate as freely in the liquid as they do in the gas, stick on every collision. On the other hand the ratio of the rotational partition function in the liquid to the rotational partition function in the gas, which Kincaid[20] and Eyring called the free angle ratio, δ, is equal to the condensation coefficient, $\varkappa$, for molecules not having free rotation in the liquid. This interesting result was noted first by George Wyllie.[21] Table III, which is part of a table of Mortensen and Eyring's[22] indicates how nearly the purely thermodynamic factor, δ, agrees with the kinetic factor, $\varkappa$.

TABLE III

	CCl_4	C_6H_6	$CHCl_3$	CH_3OH	C_2H_5OH	H_2O	$n-C_3H_7OH$
δ	1.02	.86	.26	.034	.019	.022	.008
$\varkappa$	1.	.85—.95	.16	.045	.024	.036	.037

If a molecule when it collides with a surface transfers translational energy on each collision but adjusts its rotation comparatively infrequently then $\varkappa$ should measure the fraction of molecules which can pass adiabatically, as far as rotation is concerned, from liquid to gas. But since in calculating δ, bulk rotation was used, whereas in collision the rotation of the surface layer is important one must suppose that the surface layer has a rotational partition

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

function much like the liquid interior. This again argues for a surface layer with rotational properties much like the liquid in bulk. That molecules in liquids do not transfer rotational energy at every collision follows from the fact that the thermal conductivity involves only the specific heat of translational degrees of freedom.

Surface Viscosity

The most striking thing about the surface viscosity of films of fatty acids on water is their sensitivity to pH, age of the water and age of the film. As Langmuir notes a little Ca^{++} ion can tie chains together and make the film much more solid-like. These results are exciting because of their significance for biological membranes as well as for themselves. Moore and Eyring[23] were able to apply the same theory used for bulk viscosity to explain the observed results. The much bigger heats of activation for viscous flow of films than for the same molecules in bulk is understandable in terms of combination of the molecules of the film with water or with ions thus involving the migration of bulkier aggregates. Criddle[24] has provided an interesting review of surface viscosity. Much more remains to be learned about surface properties by both theoretical and experimental studies of viscosity.

Space Charge Vibrations as a Source of Electromagnetic Waves in the Range of Audio Frequencies

The improvements in long wave length reception up to audio frequencies opens up some interesting new possibilities. A simple calculation shows that such signals should be detectable and J. A. Lasater informs me he has built an antenna which detects signals in the 2100 cycle range.

A surface bathed in a fluid containing ions will usually preferentially absorb ions of one sign or the other. Settling of charged particles under gravity as well as other types of charge separation can build up charges up to dielectric break down which may reach $E = 30{,}000$ volts per cm.

Using the equation for a condenser

$$E = \frac{4\pi n 4.8 \times 10^{-10}}{\varepsilon} \tag{3}$$

where the voltage gradient E in electrostatic units becomes $30{,}000/300 = 100$. The dielectric constant ε has the value unity. Substituting these values in equation (3) gives $n = 1.7 \times 10^{10}$ for the number of charges per unit area of the condenser which we may assume is a rough measure of charge density at break down. Classical electromagnetic theory gives for the quantity of radiation per second, Q, emitted by n oscillating particles the value

$$Q = 2/3 n \frac{e^2 a^2}{c^3} \tag{4}$$

Digitized by Google Original from UNIVERSITY OF MICHIGAN

where e, a and c are the charge of an oscillating particle, its acceleration, and the velocity of light respectively. We consider the amount of radiation to be expected due to agitation of the space charge by a sound wave of moderately high intensity at 2100 cycles. At room temperature the velocity of sound is approximately 3.3×10^4 cm/sec so that a wave length at 2100 cycles is 14 cm. Consider a sound of sufficient intensity that charged particles in the air move on the average with an amplitude corresponding to one-tenth the sound wave length or 1.4 cms. The position X of such a particle is given by the expression $X = 1.4 \sin 2\pi 2100\, t$ so that

$$a = X = -1.4(2\pi 2100)^2 \sin 2\pi 2100\, t$$

and

$$a = X = -1.4(2\pi 2100)^2 \sin 2\pi 2100\, t$$

and remembering that the mean value of $\sin^2 2\pi 2100\, t$ is 1/2 one has for the mean square of the acceleration

$$\overline{a^2} = 2\times10^{15} \text{ cm/sec.}$$

This gives $Q = 2\times10^{-25}$ ergs/sec emitted by the $n = 1.7\times10^{10}$ particles in a c.c. Now the black body radiation emitted per second from a 1 c.c. sphere at 300°K in a band width $dv = 5$ cycles at 2100 cycles is

$$Q = 4CE_\nu\, dv = 4C\frac{8\pi\nu^2\, dv}{C^3}kT = 5\times10^{-26} \text{ ergs.}$$

The 4 in the expression for Q is the surface area of a 1 c.c. sphere. It will apparently be possible to study the radiation due to all sorts of mechanical vibrations of many types of space charge over a wide frequency range. This should greatly extend our understanding of surface behavior.

Impressions of Langmuir

In the Spring of 1933 H. S. Taylor and I took about 10 c.c. of rather pure D_2O, which we had prepared electrolytically at Princeton, to the Philosophical Society Meeting in Philadelphia. This excited general interest. After our talk Dr. Langmuir invited me for a walk through the park near Independence Hall. I found him genial and interesting to talk with. In fact it was much like visiting with an old friend. Again in the Fall of 1937 at the British Association for Advancement of Science Meeting in Nottingham H. S. Taylor took Langmuir, another chemist and myself for a half day car ride through the English countryside. Here again Langmuir throughly enjoyed the lovely hills and forests and everyone had a wonderful day.

A year before we got into the last world war W. K. Lewis of M.I.T asked me to serve on a preparedness committee on which Langmuir also served. My assignment was to make sure that our gas masks would not fail to protect against some particularly penetrating smoke. Use of the new electron microscopes soon resolved the matter. Because Langmuir was also concerned with

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

smokes I had occasion to spend a day with him in his laboratory at Schenectady. This I found pleasant in every way and in the evening we had dinner together. During the dinner we discussed foreign policy and in the course of the discussion vigorously disagreed on some points which have long since been resolved. I found out that this famous scientist who sailed his own boat and piloted his own plane also held his own political opinions. It was pleasant to feel that the scientific defense of the nation' was in strong hands. In Langmuir experimental skill, intelligence and inflexible courage made success certain. Whatever the odds Irving Langmuir met the world head on.

HENRY EYRING

References

1. G. N. LEWIS: *J. Chem. Phys.*, **38**, 762 (1916).
2. *Ann. Phys.*, **49**, 4, 229 (1916).
3. H. EYRING and M. B. WALLENSTEIN: *Proc. of Natl. Acad. of Sci.*, **39**, 138 (1953).
4. R. C. TOLLMAN: *The Principles of Statistical Mechanics*, Oxford University Press, 1938.
5. G. GENTILE: *Nuov. Cim.*, **17**, 493 (1940).
6. J. FRENKEL: *Wave Mechanics*, 2nd ed., Oxford University Press, 1936.
7. R. B. RANSOM, M. B. WALLENSTEIN, B. J. ZWOLINSKI and H. EYRING: *Catalisis*, **2**, 255 (1955) Reinhold Pub. Corp. Edited by P. H. Emmett.
8. PETER T. LANDSBERG: *J. Chem. Phys.*, **21**, 2228 (1953).
9. L. BRILLUOIN: *Compt. rend.* **184**, 589 (1927); *Ann. Phys.*, **7**, 315 (1927); *Die Quantenstatistic Springer*, Berlin (1931) p. 165 ff.
10. H. EYRING, T. REE and N. HIRAI: *Proc. Nat. Acad.*, **44**, 683 (1958). I.
11. J. FULLER, T. REE and H. EYRING: *Ibid.* **45**, 1594 (1959). II.
12. T. R. THOMSON, H. EYRING and T. REE: *Ibid.* **46**, 336 (1960). IV.

12a. C. M. CARLSON, H. EYRING and T. REE: *Ibid.* **46**, 649 (1960). V.

13. C. M. CARLSON, H. EYRING and T. REE: *Ibid.* **46**, 333 (1960). III.
14. J. WALTER and H. EYRING: *J. Chem. Phys.*, **9**, 393 (1941).
15. J. D. BERNAL: *Proc. Roy. Instn.*, **37**, No. 168 (1959); *Nature*, **183**, 141 (1959).
16. T. L. HILL: *J. Chem. Phys.*, **29**, 141 (1952).
17. J. C. HENNIKER: *Rev. of Mod. Phys.*, **21**, 322 (1949).
18. N. K. ADAM: *Physics and Chemistry of Surfaces*, Oxford University Press, London (1941) pp. 5–6.
19. J. H. HILDEBRAND and R. L. SCOTT: *The Solubility of Nonelectrolytes*. Reinhold Publishing Corp. (1950).
20. J. F. KINCAID and H. EYRING: *J. Chem. Phys.*, 6, 620 (1935).
21. G. WYLLIE: *Proc. Roy. Soc.* (London), A **197**, 383 (1949).
22. E. M. MORTENSEN and H. EYRING: *J. Phys. Chem.* (in press).
23. W. J. MOORE and H. EYRING: *J. Chem. Phys.*, **6**, 391 (1938).
24. D. W. CRIDDLE: *Rheology Theory and Applications*, Vol. III, Chap. 11, Academic Press, N.Y. and London, Edited by F. R. Eirich.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

PART 1

FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS

PART I. SOLIDS

Journal of the American Chemical Society
Vol. XXXVIII, No 11, 2221, November (1916).

THE IMPORTANCE of the work of W. H. Bragg and W. L. Bragg in its bearing on chemistry has not, as yet, been generally recognized. In hearing two of W. H. Bragg's lectures in this country a few years ago, the writer was impressed with the very great significance of this work in the field of chemistry. The structure of crystals as found by the Braggs leads to new and more definite conceptions as to the nature of chemical forces.

The writer has constantly endeavored to apply this new conception in his work on heterogeneous reactions and particularly in connection with a study of the phenomena of adsorption and surface tension. In this way he has gradually been led to form more or less definite theories of the mechanism of evaporation, condensation, liquefaction, adsorption, and capillary phenomena. According to this theory, both solids and liquids consist of atoms held together entirely by *chemical forces*. The conception of the molecule thus almost entirely loses its significance except in the case of gases. In fact, we may well look upon any solid or liquid body as constituting a single large molecule. Any change of phase, such as the melting of a solid, is thus a typical chemical reaction. The mobility of liquids, according to this viewpoint, is due to a kind of tautomerism.

The present paper is merely an outline of this theory. The more detailed description of the experimental work upon which it is largely based, will be reserved for future papers.

Structure of Crystals

The idea that a crystal should constitute an effective diffraction grating for X-rays originated with Laue[1], who also saw that by means of such a grating not only could the wave length of the X-rays be determined, but also a powerful method for studying the structure of crystals was made available. The

[1] *Sitzb. d. Bayer. Akad. d. Wiss.*, June, 1912.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

detailed theory developed by Laue proved incorrect in certain important respects. W. L. Bragg[1] called attention to these errors and gave a theory by which the true structure could be determined from the diffraction pattern. Since then the method has been greatly simplified, so that at present it is usually a matter of no great difficulty to find the exact arrangement of the atoms in a crystal. In this way the structures of some 30 or more kinds of crystals have been determined.

The alkali halides NaCl, KCl, KBr, and KI all have a similar structure in which the *atoms* are arranged according to a simple cubic lattice. Thus, in the case of sodium chloride crystals, sodium and chlorine atoms alternate along three sets of lines at right angles to each other. Each sodium atom is surrounded by six equidistant chlorine atoms arranged around it, as the corners of an octahedron are arranged around its center. Similarly, each chlorine atom is surrounded by six equidistant sodium atoms.

Up to this time it had been taken for granted that crystals were built up of molecules. But from this work of the Braggs it is clear that in crystals of this type the identity of the molecules is wholly lost, except in so far as we may look upon the whole crystal as composing a single molecule. From the arrangement of the atoms we must conclude that the forces holding the crystal together (cohesion) are forces which exist directly between sodium and chlorine atoms. Every chemist looks upon such forces as chemical in nature.[2]

But the significance of this structure for the chemist extends further. Sodium is invariably regarded as a monovalent element, yet in the sodium chloride crystals we see a structure which in no wise suggests the monovalent character of the atom. The sodium atom is held by chemical forces to six chlorine atoms. If we retain the conception of valency in such a case, we must clearly admit that the valency of the sodium is divided equally between the six chlorine atoms.

If a sodium chloride crystal evaporates at high temperature, the atoms leave the surface in pairs in the form of sodium chloride molecules. These molecules are formed in the process of evaporation, since they do not exist as such in the crystal. The process of evaporation is thus a chemical process.

In the diamond, each carbon atom is surrounded by four others equidistant from it. These are arranged around the central one in the same

---

[1] *Proc. Camb. Phil. Soc.* **17**, 43 (1912). The subsequent papers of W. H. and W. L. Bragg were published in 1913 and 1914 in the *Proc. Camb. Phil. Soc.*, the *Proc. Roy. Soc.*, and the *Phil. Mag.* All of these papers were translated into German and were published together in one volume of the *Z. anorg. Chem.* **90** (1914).

[2] Of course all chemical forces are probably of electromagnetic origin, but for this reason we do not need to call the forces in crystals by the vague term "physical forces" (and thus distinguish them from chemical force).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

way as the corners of a regular tetrahedron are arranged around its center. In this case the tetravalent character of the carbon atom manifests itself clearly. When a model of a diamond crystal is examined, it is seen that the atoms appear to be arranged in rings of six, corresponding to the benzene ring. The remarkable strength of the carbon chain and especially the stability of the benzene ring, so familiar to chemists, is thus seen to be cause of the hardness, the high melting point and the low vapor pressure of the diamond.

It is interesting to note that the structure of zinc blend, ZnS, is very similar to that of the diamond, the zinc and sulfur being alternately substituted for adjacent carbon atoms. Thus each zinc atom is surrounded by four symmetrically placed sulfur atoms, while each sulfur atom is surrounded by four zinc atoms. The valency is thus again divided.

With fluorite, CaF_2, each fluorine atom is surrounded by four symmetrically placed calcium atoms, while each calcium atom has eight fluorine atoms arranged around it like the eight corners of a cube about the center of the cube.

The structure of pyrites, FeS_2, is much more complicated. Each iron atom has four equidistant sulfur atoms around it, but there are other sulfur atoms at distances only slightly greater. Similarly, each sulfur atom has three equidistant iron atoms forming a triangle around it, but above and below the plane of this triangle there are other iron atoms whose distance is only slightly greater.

Hauerite, MnS_2, has a similar structure to that of pyrites.

In the case of calcite, $CaCO_3$, the carbon and oxygen atoms lie in planes perpendicular to the crystal axis. Three oxygen atoms are arranged in groups around each carbon atom, forming an equilateral triangle. The calcium atoms lie in planes just above and just below the carbon-oxygen planes. Each calcium atom has six equidistant oxygen atoms around it. The distance between the calcium and the carbon atoms is considerably more than either the distance between oxygen and carbon, or between oxygen and calcium. Thus the crystal is evidently held together by forces acting between carbon and oxygen and between oxygen and calcium. The group CO_3 appears as a unit, since each carbon atom is associated with three oxygen atoms while these are associated with only the one carbon atom. But each CO_3 group is equidistant from six calcium atoms, so that it is impossible to pick out any of these as forming a molecule with the CO_3. If we are to retain the idea of a molecule at all, we must consider that the entire crystal is a single molecule.

In dolomite, $CaMgCO_3$, the structure is exactly similar except that calcium and magnesium planes alternate. The structures of rhodochrosite, $MnCO_3$, siderite, $FeCO_3$, and sodium nitrate, $NaNO_3$, are like that of calcite. This last case is of special interest to the chemist, since a monovalent atom replaces a divalent, and a pentavalent (?) atom replaces a tetravalent one without causing a change in the arrangement of the atoms.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The crystals of magnetite afford an illustration of a structure in which different atoms of the same element have different functions. Two-thirds of the iron atoms occur in positions in which each is surrounded by four oxygen atoms (tetrahedral arrangement), while the other third of the iron atoms are each surrounded by six oxygen atoms. The iron atoms have thus a divalent and trivalent character, but each unit of valence is divided between two oxygen atoms. Spinel, $MgAl_2O_4$, has an exactly similar structure in which the Mg atoms take the place of the divalent iron atoms, while the Al atoms replace the trivalent iron atoms.

Crystals of metallic copper and metallic silver have been found to have their atoms arranged according to the face-centered cubic lattice. This arrangement is the same as the familiar one obtained when round shot are piled in layers as regularly and compactly as possible. In this structure each atom is equidistant from the twelve adjacent atoms.

The structures of crystals of rhombic sulfur and quartz have been partly worked out. In the sulfur crystals the atoms are found to be arranged in a lattice structure in groups of eight. The particular arrangement of the atoms within these groups is not yet known. To the chemist it is of significance that these groups of eight contain the same number of atoms as are found in molecules of sulfur vapor. Here, then, for the first time, the crystal has a structure in which the identity of the molecules (as found in the gas phase) is apparently not wholly lost.

In recent article[1] L. Vegard shows that the structures of gold and lead crystals are the same as those of silver and copper. He also describes the structure of the zircon group of minerals represented by zircon, $ZrSiO_4$, rutile, TiO_2, and cassiterite, SnO_2. The structure of zircon proves to be especially interesting, for it is found "that each of the Zr or Si atoms is associated with two oxygen atoms; thus the groups SiO_2 and ZrO_2 form a kind of 'molecular elements' of the lattice. This is not merely a way of regarding the geometrical arrangement of the atoms; but we have reason to believe that the groups SiO_2 and ZrO_2 form chemically saturated compounds" within the crystal.

Two facts stand out clearly as a result of the consideration of these crystal structures. In the first place, it is evident that crystals are built up of atoms in such a way that each atom is chemically combined to all the adjacent atoms, while these in turn are combined to those beyond.

Secondly, we see that the arrangement of the atoms in general does not follow the usual rules of valency, but that each atom is combined with a much larger number of atoms than corresponds to its normal valence.

In the past it has been customary to consider that solids and liquids are held together by the "forces of cohesion" and to call these "physical forces" as distinguished from chemical forces. Often these distinctions are known to be rather vague, but in the more recent years, with growing confidence in

[1] *Phil. Mag.* **32**, 65 (1916).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the atomic theory, we have been accustomed to consider that chemical phenomena are those involving an alteration of the structure of molecules, while physical phenomena are those in which only the molecule as a whole is concerned. This distinction throws the whole difficulty back on to the definition of the molecule. In gases there is usually no uncertainty as to the size of the molecules, but in liquids and solids no really satisfactory methods have been found for determining molecular weights. As long as we cannot definitely determine the molecular weights, it thus remains impossible to distinguish sharply between chemical and physical phenomena. Nevertheless, much discussion has arisen of late years over such questions as whether adsorption and surface tension are chemical or physical phenomena. The overwhelming consensus of opinion seems to be that these are both physical phenomena.

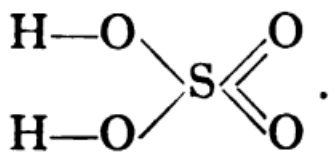
In the following pages the writer hopes to show that there is no present justification for this distinction between chemical and physical forces. Cohesion, adsorption and surface tension are all manifestations of forces similar in their nature to those acting between the atoms of solid bodies. It is therefore advantageous to look upon these forces as direct results of chemical affinity. In this way it becomes possible to correlate these so-called physical phenomena with the known chemical characteristics of the atoms and groups of atoms forming the bodies.

Theories of Chemical Constitution

The fact that each atom in a crystal is usually combined with a larger number of adjacent atoms than corresponds to its valence, is not in conflict with recent theories of the constitution of chemical substances.

A. Wener[1] has made a very extensive study of complex inorganic compounds, and as a result has established a theory of residual or secondary valence.

In accordance with the ordinary theory of valency which has proved so invaluable in organic chemistry, it has been customary to assign structural formulas of similar type to inorganic compounds. Thus the graphic formula for sulfuric acid is often written



Whereas among organic compounds the structural formulas can be determined with certainty and undoubtedly correspond to the actual arrangement of the atoms in the molecules, no such certainty is ever found in the case of complex inorganic compounds. As a result, such formulas have served no useful purpose in the development of inorganic chemistry. In fact, Werner claims that the common acceptance of such conceptions was responsible for the fact that our knowledge of the constitution of inorganic compounds failed to progress for so many years.

[1] *Neuere Auschauungen auf dem Gebiete der Anorganischen Chemie*, Braunschweig (1905).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Werner[1] then shows clearly that such formulas are untenable. In the first place, the formula would lead to a sharp distinction between the combination of oxides and halides, whereas such a distinction does not actually exist. A proper theory should show a close relationship between such reactions as

$$K_2O+SO_3 = K_2SO_4$$

and

$$KCl+AuCl_3 = KAuCl_4.$$

The same kind of relations exist with complex cyanides, nitrites, etc., and these cannot be accounted for by the ordinary theory of valency.

Secondly, the ordinary theory would indicate that oxides such as OsO_4, RuO_4, etc., should easily form acids by combination with water. Actually, it is found that the number of molecules of water which can be taken up by an oxide does not bear any definite relation to the number of doubly bound oxygen atoms.

Several other good reasons are given against the ordinary graphic formula for such compounds.

Werner then proceeds to show that the ordinary conception of (primary) valence applies (except in organic compounds) practically only to compounds of the first order; that is, to simple compounds containing not more than two elements, such as H_2O, NaCl, SO_3, etc.

Compounds of higher order are formed when compounds of the first order combine together. Thus Werner draws no sharp distinction between the combination of P_2O_5 and Na_2O to form Na_3PO_4, and such a process as the taking up of "water crystallization" by a salt such as $BaCl_2$ to form $BaCl_2.2H_2O$.

When two elements combine to form a compound of the first order, their primary valences become saturated. But there is still a field of force around the molecule which enables it to combine with other molecules to form compounds having almost any degree of stability. The molecules are then said to be held together by residual or secondary valence.

Werner gives the following definitions of primary and residual valency:

(*a*) "Primary valence serves to unite those simple or complex radicals which can exist as separate ions or whose chemical combining power is equivalent to an ionizable radical."

(*b*) "Residual valence represents the affinity that binds together radicals which can neither act like nor be equivalent to separate univalent ions."

As illustrations of primary valence, he gives $-Cl$, $-Na$, $-NO_2$, $-CH_3$, and for residual valence: OH_2, $:NH_3$, $:ClK$, and $:CrCl_3$.

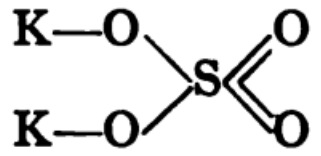
R. Abegg[2] advanced a somewhat similar theory of the constitution of inorganic compounds. He looks upon salts of oxygen acids, for example, as consisting of basic and acid oxides held together by secondary valence. He considers

[1] *Loc. cit.*, p. 42.

[2] *Z. anorg. Chem.* **39**, 330 (1904); **50**, 309 (1906), and *Z. physik, Chem.* **69**, 1 (1909).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Berzelius' idea of the structure of such compounds ($K_2O.SO_3$, for instance) to be much preferable to the structural or graphic formula



and gives many good reasons to support his contention.

Stark[1] has developed a theory of the mechanism of chemical valency based on the electron theory. This electroatomic theory gives symbolically a very satisfactory picture of the different types of valence. According to Stark, portions of the surfaces of atoms contain an excess of positive electricity. In the neutral atom one or more electrons are held close to the surface of the atom by this positive charge. Compounds are formed when the lines of force from one of these "valence electrons" reach out and end on the positive areas of other atoms. In the case of strongly polar compounds, an electron is almost wholly drawn over to the atom which it holds in combination. Primary valences are due to a pair of valence electrons whose field binds two atoms together. The stray electric field in the space around the resultant molecule is the cause of the residual valence. This theory accounts particularly well for the gradations between primary and secondary valence.

Thus when two atoms combine chemically, they are held together by certain electrons which are common to both atoms. Bohr's model of the hydrogen molecule assumes a similar function of the electrons. According to Bohr's theory, a hydrogen atom consists of a positive nucleus around which (at a distance of 0.55×10^{-8} cm) an electron revolves with very high speed. The hydrogen molecule, on the other hand, consists of two hydrogen nuclei (at a distance apart of 0.60×10^{-8} cm) and two electrons which revolve in an orbit in a plane perpendicular to the line joining the nuclei. The radius of the orbit of the electrons is 0.52×10^{-8} cm. In the hydrogen atom the electron forms part of the atom. When two atoms combine the two nuclei share the two electrons equally. If the two atoms separate again, there is an even chance that they will have exchanged electrons. The two electrons held in common by the two nuclei hold to molecule together and are thus equivalent to the bond by which we ordinarily imagine two univalent atoms to be jointed. This model of the univalent bond is remarkably similar to that proposed by Stark.

J. J. Thomson[2] has also developed a theory of the mechanism of chemical affinity. On the whole, his theory is very much like that of Stark. Thomson considers that the electrons near the surface of an atom, together with the

---

[1] *Jahr. d. Radioakt. und Elek.* **5**, 125 (1908); *Prinzipien der Atom dynamik*, Vol. 3; *Die Elektricität im chemischen Atom*, Leipzig, 1915. A short description of Stark's theory of valence was given by Misses Hahn and Hölmes in *J. Am. Chem. Soc.* **37**, 2611 (1915). This article is essentially an abstract of Paul Ruggli's book, *Die Valenzhypothese von J. Stark vom Chemischen Standpunkt*, Stuttgart, 1912.

[2] *Phil. Mag.* **27**, 757 (1914).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

positive charge in the core of the atom, constitute one or more electric doublets which exert forces not only on free electrons or ions in their neighborhood, but also on other electric doublets. The force of attraction between such doublets varies much more rapidly with the distance than the inverse square. Thomson uses the dielectric constant of the substance in the gaseous condition as a measure of the moment of the electric doublets. In this way he concludes that there has been an actual transfer of an electron from one atom to another in such compounds as H_2O, NH_3, SO_2, HCl, CH_3OH, C_2H_5OH and CH_3Cl, even when these are in the gaseous condition. This "intramolecular ionization" greatly increases the moment of the doublet by increasing the distance between the charges. In other types of compounds, however, Thomson believes that the atoms are electrically neutral and are held together by one or more doublets on each atom. As compounds of this type he cites H_2, O_2, N_2, Cl_2, CO, CO_2, CS_2. CCl_4, C_6H_6, CH_4, N_2O.

It should be noted that Stark's theory recognizes both these types and indicates how there may be all possible gradations between these extremes.

Thomson also believes that the more complex compounds are "molecular compounds" in which simple molecules are held together by the stray field around the molecules. In the first paragraph of his paper he says: "These forces will be exerted by the atom not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules and producing thereby the intrinsic pressure and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin, but acting between the atoms of the same molecule."

We shall see that this division of solids and liquids into molecules is very arbitrary and that the same kind of chemical relationships exist between these forces, which Thomson calls physical, as exist among the forces which cause the formation of molecular compounds.

In regard to saturated valence, Thomson considers that two electrons are involved in holding two univalent uncharged atoms together. In this respect his theory is like those of Stark and Bohr. He points out, however (as Stark has also done), that by this theory three univalent atoms may be held together in the form of a ring, one electron being located between each pair of adjacent atoms. He says: "The difference between the theory we are considering and the accepted theory of valency may be expressed by saying that not only is every possible valency compound on the old theory a valency compound on this theory, but every compound which would be a valency one on the old theory if the valency of every element was doubled, would be a valency compound on the new, with the atoms retaining their original valency. This only

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

applies to the compounds when the atoms are uncharged; when the atoms are charged the valency conditions are the same as on the old theory."

This theory would seem to fit in badly with the facts of organic chemistry, for we find no evidence of organic compounds in which carbon acts as if it had a valency of eight or hydrogen a valency of two. But in the formation of crystals this theory suggests an explanation of the divided valence observed in crystals of the spinel group. For instance, it was found in magnetite that the *di*valent iron atoms were surrounded by *four* symmetrically placed oxygen atoms, while the *tri*valent iron atoms were surrounded by *six* oxygens.

An extremely important theory of the "Atom and Molecule" is that recently described by G. N. Lewis[1]. Substances are classified into two general groups: polar and nonpolar. The polar type, represented by H_2O, NH_3, NaCl, etc., is characterized by reactivity, high dielectric constant, tendency to form molecular complexes, etc. Tautomerism is a "predominant trait of most inorganic substances (polar type), which behave as if a great variety of forms were existing together in extremely mobile equilibrium."

For this reason Lewis[2] believes that the constitution of the more complex inorganic compounds cannot be represented by any single structural formula.

We shall see that these ideas on tautomerism will prove of value in connection with a study of the constitution of liquids.

Crystal Structure from the View Point of Chemical Theory

The work that has been done so far on crystal structure testifies to the general applicability of such theories of chemical constitution as that of Werner.

Except in the case of diamond crystals, no structural formula can be written consistent with our ordinary ideas of (primary) valence, which adequately represents the constitution of the crystal. We see, however, that the arrangement of the atoms in crystals is just what we should expect if the forces binding the atoms together are similar to those forces which, by Werner's theory must hold together the *molecules* in molecular compounds (compounds of higher orders).

Werner's theory, however, needs to be modified in some respects, to fit in with the new work. According to Werner, compounds of the first order are held together by primary valence, and only when these simple compounds form compounds of higher orders are the residual valences called into play. But when we consider the structure of the halide salts of the alkalies and the structure of such crystals as fluorite, we must conclude that even in the case of these first order compounds the ordinary rules of valence do not always apply.

It thus seems that secondary, or residual valence is active, not only in the higher order compounds, but that a valency of the secondary type may also characterize single atoms when these are combined with others in crystals.

---

[1] *J. Am. Chem. Soc.* **38**, 762 (1916).

[2] *J. Am. Chem. Soc.* **35**, 1448 (1913).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

It is evident that solid bodies could not be built up of atoms held together exclusively by primary valences except in the case of atoms having valences of four or more. Thus, when two monovalent atoms combine to form a gas molecule, they are held together by primary valence. If there were no residual valence, these molecules could not condense either as a solid or liquid. Divalent atoms could combine together in long chains, but these chains could not be linked together except by secondary valence. With trivalent atoms branching chains could be formed which could interlock so as to cover a plane surface, but except by secondary valence no atoms could be held outside of this plane. With tetravalent atoms, on the other hand, the atoms can be linked together by their primary valences, as in the diamond crystal, so as to fill a volume.

We thus see that primary valences cannot play an important part in crystal structure in the case of atoms with a valency of less than four. Most of the crystals containing tetravalent atoms which have been studied so far, have shown that the primary valences of the tetravalent atoms seem to exert their influence. This is shown not only in the case of the diamond, but in zircon, cassiterite and rutile, in which each atom of Zr, Si, Ti or Sn is clearly associated with two atoms of oxygen.

From these considerations it seems that in general there is a strong tendency for every atom to form compounds by means of its primary valence, but where the conditions are such that combination by primary valence is no longer possible then secondary valence is called into play and may entirely supersede the primary valence.

Thus, when sodium atoms and chlorine atoms combine at high temperatures to form gaseous NaCl, the primary valence holds the atoms together. But when the pressure is raised or the temperature is lowered, the secondary valence is enabled to completely supersede the primary valence, since the primary valence cannot cause the combination of the molecules necessary to form a solid body.

With divalent and trivalent atoms a sort of divided valence like that suggested by J. J. Thomson, is apparently often manifest and is probably a sort of transition between primary and secondary valence. This is seen particularly in crystals of the spinel group, in which the divalent atoms have assumed a tetravalent character and the trivalent atoms a hexavalent character.

By this division of each of the valence units into two parts, the apparent valency is raised to four or more, so that the solid body can then be held together by this means. According to Stark and J. J. Thomson's theories, we should never expect the subdivision of a primary valence unit into more than two parts. Furthermore, we should not expect that a monovalent element would often exhibit this divided valence in solid bodies, because, even if its apparent valence was doubled by this means, it still would not be able to make use of this valence in forming a crystal.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

The compounds whose crystal structures have been studied thus far, are all more or less of the polar type. It is not safe to conclude that the structures of nonpolar compounds will be similar to those already found.

For example, when an organic compound such as methane, is crystallized as a solid and is then converted again into a gas, it is certain, from chemical considerations, that none of the hydrogen atoms have been separated from the carbon atoms to which they were originally attached. The identity of the original molecules must, in a sense, have been preserved even when the methane was in the solid condition.

On the other hand, with crystals of the types studied so far, the substance could not be condensed from the gaseous condition and be reevaporated again without most of the atoms having exchanged partners. Thus, when a crystal of sodium chloride evaporates, a sodium atom on the surface may escape with any one of the four adjacent chlorine atoms as a molecule of salt vapor. There is only a small chance that the particular chlorine atom with which it escapes will be the same one as that with which the sodium atom was combined before it formed part of the crystal.

From these considerations we are forced to conclude that in crystals of methane each carbon atom is surrounded by four hydrogen atoms held to it by primary valences. The crystal is then held together by residual valences. Since the methane is so thoroughly saturated chemically, these residual forces are very weak and, therefore, methane melts and boils at a very low temperature. But there is absolutely no reason for assuming that these residual forces are any less chemical in nature than those which cause the combination of K_2O and SO_3 to form K_2SO_4. We certainly cannot limit chemistry to a study of only those substances whose atoms are held together by primary valence.

Determination of the crystal structure of organic compounds should prove of very great value in clearing up the true distinctions between primary and secondary valence. Unfortunately, the very low absorption of X-rays by the hydrogen makes it difficult to determine the positions of the atoms of this element by the present methods. This difficulty can be avoided by choosing such substances as C_2Cl_6 and C_6Cl_6.

Similar considerations to those used with methane apply to such substances as H_2, N_2, O_2, etc., and nearly all typical organic substances. That the crystal structure, even with these substances, depends on the space arrangement of the atoms, is clear from the work of W. Wahl[1] on the crystal forms of the lower members of the aliphatic hydrocarbon series. He finds methane crystallizes in the isometric system, ethane in the hexagonal, propane apparently rhombic, trimethyl methane probably rhombic. Tetramethyl methane occurs in two modifications, one isometric and one tetragonal. Normal butane also has two forms, hexagonal and rhombic. Normal pentane is rhombic, while normal hexane, heptane and octane are monoclinic or triclinic.

[1] *Proc. Roy. Soc.* (A) **88**, 354 (1913).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The lower members of this series show a remarkable agreement between the chemical constitution and the crystal form. Thus the symmetry of the methane molecule requires a crystal of the isometric form, probably with an arrangement rather similar to that of the diamond. If we look upon the carbon atom as having its bonds arranged symmetrically after the pattern of the tetrahedron, then the ethane molecule would consist of two carbon atoms each with three hydrogen atoms (in planes 120° apart) arranged around them. This leads naturally to the hexagonal form.

The definiteness of this dependence of the crystalline form upon the arrangement of the atoms indicates that even with these nonpolar compounds the forces holding the ***molecules*** together in the crystals are of the same nature as those holding the ***atoms*** together in the polar types of crystals.

Since the forces acting between the molecules in these crystals are then quite similar to those acting in the more complex inorganic compounds we would still be justified in regarding a crystal of methane as one large molecule. We thus have molecules within the molecule.

This leads us to consider whether it is not desirable to revise our conception of the molecule. There is an advantage in looking upon every crystal (and in fact every mass of liquid) as a single large molecule, in that this viewpoint brings out strongly the *chemical* nature of the forces holding the crystal together, and thus encourages us to apply to the study of these forces the knowledge already available from other fields of chemistry.

On the other hand there is a real need for a term to denote a group of atoms which can pass from the gas phase to the solid (or liquid) and back again without the exchange of any atoms. If, however, we should limit the word molecule (in liquids and solids) to this narrow definition, we would have to say that there are no molecules at all in the great majority of inorganic substances.

On the whole, it seems best to define a molecule as *a group of atoms held together by atomic forces*. We must then distinguish between various kinds of molecules.

The *gas molecule* may be defined in terms of Avogadro's Law, and is thus only sharply definable in so far as the gas follows the laws of ideal gases. We may define a *fixed molecule* as the largest aggregate of atoms which may pass from the gaseous phase to the solid (or liquid phase) and back again to the gaseous phase without exchange of atoms with other aggregates. With substances which are wholly nonpolar, such as the saturated hydrocarbons, this definition of fixed molecule is probably never ambiguous. But with molecules which are partly polar, as for example acetic acid, this definition may lack sharpness. Thus when CH_3COOH vapor dissolves in water (or condenses as a solid), it is probable that the replaceable hydrogen atom will be exchanged with that of the other CH_3COO groups. According to our definition of fixed molecule we must, therefore, consider that the *fixed molecules* in liquid or solid acetic acid consist of CH_3COOH groups. Cases will frequently arise, as for example

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

in the alcohols, where the rate of exchange of the hydrogen atoms is so slow as to be almost negligible, so that it will be impossible to limit sharply the extent of the fixed molecule. This difficulty, however, seems an inherent one, for it depends upon the fact that all possible degrees of tautomerism may actually exist in the large molecule forming the whole mass of the solid or liquid.

It will also be convenient to distinguish another type of molecule which we may call the *group molecule*. This may be defined as an aggregate of atoms which are interrelated in such a way (by position or mobility) that the atoms in the group may be distinguished from atoms outside the gruop. Thus in solid methane each hydrogen atom is associated with a particular carbon atom, while the carbon atom is associated with four hydrogen atoms. All other hydrogen atoms beside these four may be distinguished from these by their being combined with a different carbon atom.

If we represent a methane crystal diagrammatically as follows:

```
  H     H     H
 HCH   HCH   HCH
  H     H     H
  H     H     H
 HCH   HCH   HCH
  H     H     H
```

it is evident that we might also look upon the crystal as consisting of group molecules of hydrogen (H_2) held together by carbon atoms. Chemical considerations, however, would lead us to choose CH_4 as the group molecule.

In liquid methane we could distinguish the group molecule either by the fact that four atoms of hydrogen must be geometrically associated with a single carbon atom, or by the fact that four hydrogen atoms always move with a particular carbon atom, whereas all other neighboring hydrogen atoms in the course of time gradually (by diffusion) become separated more and more from the given carbon atom.

A crystal of zircon would thus be a compound consisting of group molecules of ZrO_2 and group molecules of SiO_2.

In inorganic compounds in the solid or liquid state there are usually no fixed or group molecules. It is probable, however, that an ion of the type CO_3^{--} in solution constitutes a group molecule, since the structure of the calcite crystal suggests the carbon atom may be more or less permanently associated with three particular oxygen atoms. An ion of the type OH^-, however, can probably not be properly looked upon as a group molecule since the high mobility of the OH^- ion and other factors indicate that this ion is continually exchanging its atoms with the surrounding mass of water.

Besides these types of molecules, there are the large molecules which constitute colloid particles. These may be called *colloid molecules*. They probably usually consist of large aggregates of atoms or group molecules combined

Digitized by Google Original from UNIVERSITY OF MICHIGAN

together by means of secondary valence. In the second part of this paper the probable structure of these colloid molecules will be discussed in more detail.

Finally, every continuous solid or liquid mass whether homogeneous or not may be looked upon as consisting of one large molecule. We may speak of molecules of this type as *solid* or *liquid molecules.*

Forces between Atoms in Crystals

From our knowledge of the structure of crystals and from such properties as specific heat, compressibility, thermal coefficient of expansion, elasticity in different directions, melting point, vapor pressure, and latent heat of evaporation, it should be possible to determine the laws governing the forces around the atoms. Such a study would give us the clearest kind of insight into the nature of chemical affinity.

In view of the marked influence of temperature on the properties of liquids and solids, it is evident that the motions of the atoms in solids are of great importance. A study of specific heats gives us considerable information regarding the kinetic energy of the atoms. According to the Principle of the Equipartition of Energy[1] the average kinetic energy of any particle is $1/2\ kT$ for each degree of freedom, where k is the Boltzmann gas constant and is equal to 1.372×10^{-16} ergs per degree. In other words, each particle should contribute the amount $1/2\ k$ to the specific heat for each degree of freedom which it possesses. Thus for a gram molecule of particles (6.06×10^{23}) we find a specific heat of 1/2 R for each degree of freedom. Here R is the gas constant ($6.06\times10^{23}\times1.372\times10^{-16} = 83.1\times10^{6}$ ergs/deg.). Expressed in calories this gives 0.993 calorie per degree per gram atom for each degree of freedom. We thus have the simple rule that the atomic or molecular heat should be numerically equal to 0.993 times the number of degrees of freedom (n) of the atoms or molecules.

Each atom of a monatomic gas has three (translational) degrees of freedom and we should thus expect the atomic heat to be $C_v = 3\times0.9935 = 2.98$. Actually for all the monatomic gases we find exactly this value with the single exception of helium, which gives a slightly lower value.

The specific heats of most diatomic gases is approximately $C_v = 5$, from which we may conclude that there are five degrees of freedom (three translational and two rotational). The possible motion of the two atoms along the line joining them, evidently does not represent a degree of freedom. However, the diatomic gases like chlorine, bromine and iodine which are easily dissociated into atoms, have specific heats considerably greater than 5. There is thus evidence that with very strong chemical forces between atoms the number of degrees of freedom is less than with weaker forces.

---

[1] For a short description of this principle and its present significance, see Dushman, *General Electric Review*, Sept., 1914.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

The atoms of copper, silver, gold and lead are arranged according to a simple face-centered lattice with single atoms at each point of the lattice. It is evident that there are no group molecules. Each atom must possess (at high temperatures) three degrees of freedom corresponding to the directions in which it may move.

We know, however, in accordance with Dulong and Petit's law that the atomic heat of these metals is approximately 6.0,[1] and this is usually explained by assuming that the atoms vibrate in such a way that their energy is equally divided between kinetic and potential energy. When a body such as a pendulum describes *harmonic* vibrations, the time average of its kinetic energy is equal to the time average of its potential energy, if we assume that its potential energy is zero when it passes through its equilibrium position. The equipartition principle is concerned directly only with kinetic energy, but if the average potential energy is equal to the average kinetic energy it is evident that it will contribute as much as the latter to the specific heat. Thus if the atoms of the solid body describe harmonic oscillations about their equilibrium positions, the atomic heat should be double that corresponding to the three degrees of freedom, in other words, it should be $6 \times 0.9935 = 5.96$.

It is often said that in this case there are three kinetic and three potential degrees of freedom. This statement is open to serious objection, for it implies that the Equipartition Principle is applicable to potential energy. As a matter of fact, if the forces around the atoms are such as to lead to oscillations that are not harmonic in character there will in general be no equality be-

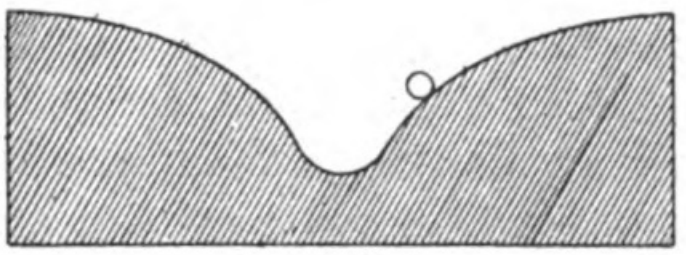


FIG. 1.

tween the time averages of the kinetic and potential energies. For example, let us consider a ball rolling on a surface, such as that represented in Fig. 1. If the ball is displaced from its lowest position and released, it will oscillate about this position. If the displacements are small the motion will be approximately harmonic in character. But with oscillations so large that the ball frequently mounts up on to the comparatively level parts of the surface,

[1] According to Dulong and Petit's Law, the atomic heats of the elements at *constant pressure* are about 6.3. The specific heat of 6×0.993 calculated by the Equipartition Principle is the atomic heat at constant volume. Lewis, Nernst, Lindemann and others have shown that the atomic heats of metals at *constant volume* gradually approach the above value assymptotically at higher temperatures, but at lower temperatures the atomic heat is considerably less. Elements with atomic weight less than about 20 form an exception to this rule in that their atomic heats are less than 6×0.993 even at room temperature.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

it is evident that the oscillations will be far from harmonic. In this case, the motion of the ball on the flatter parts of the surface will be so slow that the length of time it remains in these positions will be much larger than it would be if the slope of the surface increased steadily from the center outwards. Thus with such a surface the time average of the potential energy may be much greater than the time average of the kinetic energy.

The same considerations apply to the oscillations of atoms. If the restoring force acting on an atom is proportional to the displacement from the equilibrium position (condition for harmonic motion) then the average kinetic and potential energies will be equal and the atomic heat will be 6×0.993. But if the restoring force increases more slowly than proportional to the distance (as in the case cited above), then the potential energy will be greater than kinetic energy so that by the Equipartition Principle the atomic heat will be greater than 6×0.993. On the other hand, if the restoring force increases more rapidly than the displacement, then the atomic heat will be less than 6×0.993.

The remarkable closeness with which the atomic heats at constant volume approach the value 6×0.993 at the higher temperatures, may be taken as proof that the forces to which the atoms in solids are subjected vary approximately in proportion to the displacement of the atoms from equilibrium positions. There must then be both attractive and repulsive forces acting between the atoms. On the average, these opposing forces must just balance each other. As one atom approaches another the repulsive force must *gradually* increase and the attractive force decrease until the repulsive force greatly predominates. We cannot consider that the repulsive forces in solids are exerted only during collisions between atoms, for under these conditions there would be no potential energy and the atomic heat would be 3×0.993.

No adequate explanation has been offered of the repulsive forces between atoms. If matter is built up of positive and negative electricity the ordinary electromagnetic theory would indicate that the two opposite charges would neutralize each other. Actually, however, this neutralization only occurs to the extent of destroying the electric field at a comparatively large distance from the electrons. The positive and negative electrons are never able to destroy one another. Some cause, at present unknown, must operate to keep the positive and negative charges from approaching with less than a certain distance. It is evident that the laws govering the forces and motions of electric charges separated by distances comparable with the dimensions of atoms are in some respects radically different from the laws with which we are familiar. G. N. Lewis[1] believes that such considerations lead "irresistably to the conclusion that Coulomb's law of inverse squares must fail at small distances," and that it may be necessary to modify the law "even to the extent of changing

[1] *J. Am. Chem. Soc.* **38**, 773 (1916).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the sign of the force." This difficulty is undoubtedly connected in some way with those which have forced us to the quantum theory. Some more or less successful attempts have been made to apply this quantum theory to the structure of atoms and molecules. Bohr's theory of the hydrogen atom has been remarkably successful in that it enables one to calculate all the lines in the Balmer series of the hydrogen spectrum, but his theory of the hydrogen molecule is apparently not complete, for it leads to a value of 63,000 calories for the heat of formation of H_2 from atoms, while direct measurement[1] gives 84,000 calories.

A very suggestive theory has been worked out by A. L. Parson[2] in which he assumes that the electron itself is not merely an electric charge but is also a magnet. Crehore[3] has developed a theory in which the magnetic field produced by the rotation of electrons in extremely small orbits (10^{-12} cm) is assumed to play an essential part in the structure of molecules. By means of the magnetic fields, it is possible to account for both attractive and repulsive forces. Both of these theories assume that the positive electricity of the atom is distributed uniformly throughout a sphere of definite size, inside of which the electrons are located (Thomson's theory). Rutherford's work on the scattering of alpha particles, Moseley's work on X-ray spectra, and considerations based on the disintegration of the radioactive elements, all seem to compel us, however, to adopt Rutherford's theory of the atom in which the positive electricity is concentrated in the center of the atom and the electrons revolve in one or more orbits of diameters of the order of magnitude of 10^{-8} cm. The strength of this evidence in favor of Rutherford's theory is such that it seems to the writer impossible to accept either Parson's or Crehore's theory in their present forms.

These questions will probably be satisfactorily answered only when we understand the mechanism underlying the quantum theory and know the true relationship between positive and negative electricity. We must have an explanation of the remarkable fact that the charge on an electron is *exactly* equivalent (although opposite in sign) to the unit of positive electricity (for example the nucleus of the hydrogen atom).

At present, therefore, in an analysis of the forces between atoms, we must recognize both attractive and repulsive forces, although we cannot satisfactorily explain the mechanism of the repulsive forces. Thus by admitting the existence of forces which prevent electrons from approaching too closely to positive charges we may accept Stark's and J. J. Thomson's theories of the general character of the forces between atoms.

---

[1] Langmuir, *J. Am. Chem. Soc.* **37**, 417 (1915).

[2] "A Magneton Theory of the Structure of the Atom," *Smithsonian Publication* 2371, Washington, 1915.

[3] *Phil. Mag.* **29**, 310 (1915).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

There are many other properties of solids which indicate that repulsive as well as attractive forces exist between atoms, and that the repulsive forces act over distances comparable with the dimensions of atoms and not merely during collisions between atoms.

The compressibility and coefficient of thermal expansion are two such properties. In the case of ideal gases, these quantities vary with the pressure and temperature in a way that indicates that the volume would be zero if the atoms or molecules were brought into contact.

From the smallness of the coefficient of expansion of solids we must conclude that even at the absolute zero of temperature, the volume of crystals would not be so very much less than at room temperature. Furthermore, there are no indications that the compressibility would become zero even at the absolute zero. These facts are further evidence that the atoms of solids tend to be held in definite equilibrium positions by forces which vary approximately proportionally to the displacements of the atoms from these positions.

Nernst, Einstein and Lindemann have shown that the natural frequency of vibration of the atoms of elements may be calculated by three independent methods based, respectively, on measurements of the specific heat at low temperatures, the compressibility and the melting point. The fairly good agreement between these methods lends further support to the belief that the atoms vibrate about equilibrium positions.

The intensity of the higher orders in the X-ray spectrum of crystals, increases as the temperature of the crystal is lowered. This effect, known as the Debye effect, constitutes striking proof of the heat vibrations of the atoms and should lead to quantitative measurements of these vibrations.

The magnitude of the heat conductivity of solids, especially metals, throws some interesting light on the character of atomic vibrations. Let us imagine all the atoms in the surface layer of a solid to have their temperature suddenly raised by a given amount. This layer will then rapidly cool and will approach the temperature of the underlying layers. The rapidity with which this temperature equalization takes place will measure the rate at which a motion of one atom affects the adjacent ones. A simple approximate calculation[1] gives the time necessary for the temperature increment of the surface layer to fall to 37% of its initial value.

$$t_r = \frac{3k}{h\sigma}. \tag{1}$$

Here k is the Boltzmann gas constant 1.372×10^{-16}, h is the heat conductivity of the solid and σ is the distance between adjacent atoms. The quantity t_r is exactly analogous to Maxwell's "time of relaxation" in a gas which

[1] See Langmuir, *Phys. Rev.* **8**, 149 (1916).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

is the time needed for any abnormal distribution of kinetic energy among gas molecules to subside to $1/e^{th}$ of its original value.

For copper we thus find $t_r = 4.6 \times 10^{-16}$ seconds. This has been calculated on the assumption that each atom can receive heat from one direction only. When we consider that a single atom in the interior may receive energy from six different directions, it seems probable that the real time of relaxation of a single copper atom is about 10^{-16} seconds. Now the atomic frequency calculated from the compressibility by Einstein's method is 5.6×10^{-12}, or the time necessary for an atom to complete a single oscillation, the reciprocal of this or 1.8×10^{-13} seconds. Thus the time required for an atom nearly to reach equilibrium with its neighbors is only 1/1800th of the time of a single oscillation[1].

Even for nonmetallic substances, such as sodium chloride, the time of relaxation is always very small compared to the natural period of the atoms. This indicates that motions of a single atom must always be very highly damped. In other words, the atoms behave towards each other as though they were almost completely inelastic. However, if all the atoms are stimulated simultaneously by a periodic disturbance having a frequency corresponding to the natural frequency of the atoms, then the oscillations will be practically undamped, for there are then no adjacent atoms to which the oscillating ones can give up their energy.

We shall see that this apparent inelasticity of the atoms of solids is of great importance in the theory of evaporation, adsorption and surface tension.

The principle of the Equipartition of Energy has been found to apply at higher temperatures to the specific heats of monatomic gases, most diatomic gases and most elementary solids. But at low temperatures the specific heats always fall below that calculated by this principle. According to Einstein's theory this is due to the inability of oscillators to take up energy in quantities less than $h\nu$, where h is Planck's quantum 6.58×10^{-27} erg deg. Whether this is the correct explanation or not, it is a fact that degrees of freedom tend to disappear at lower temperatures. Eucken has shown that at temperatures as low as 58° absolute, hydrogen molecules have only three degrees of freedom, whereas they have five at ordinary temperatures. Similarly the specific heat of helium at the lowest temperatures falls even below 2.98. Evidently, therefore, it is possible that a single atom may have less than three degrees of freedom, although it is hard for us to conceive of such a possibility.

---

[1] A. H. Compton, *Phys. Rev.*, 7, 341 (1916) in a "Physical Study of the Thermal Conductivity of Solids" reached the conclusion "that the average distance through which the energy of an atomic collision in a crystal is transmitted is approximately inversely proportional to the temperature *and is many times the distance between atoms.*" In many ways this is equivalent to our conclusion that the time of relaxation is small compared to the natural period of oscillation. From what has been said above, Compton's statement is open to serious objection, since we cannot look upon the repulsive forces in solids as being due to *collisions*.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The smaller the atomic weight of an element and the greater the strength of the union between the atoms, the higher is the temperature at which the atomic heat begins to be normal (5.96). Thus there seems to be a relation between the natural frequency of the atoms and the deviations from the equipartition principle.

However, Trautz[1] attempts to explain the decrease in the specific heat of hydrogen at low temperatures by assuming that for each temperature a certain fraction of the hydrogen molecules are transferred into another modification of hydrogen which has the properties of a monoatomic gas. A. H. Compton[2] makes a somewhat similar assumption regarding solids, namely, that at low temperatures the atoms are agglomerated into larger aggregates in which the individual atoms lose one or more of their degree of freedom.

The specific heat of solids at ordinary temperatures is a distinctly additive property (Kopp's rule), a fact which is in itself an indication that solids are not built up of molecules. With compounds of the heavier elements, each atom contributes an equal amount (about 6.3 calories per gram atom at constant pressure) to the specific heat. In the case of the lighter elements, such as those forming organic compounds, the additive relations still hold fairly well, but the atomic heats of these elements must be taken to be less than 6.4. According to Kopp's rule,[3] the following atomic heats should be taken: C = 1.8, H = 2.3, B = 2.7, Be = 3.7, Si = 3.8, O = 4.0, P = 5.4, S = 5.4 and all elements of higher atomic weighs about 6.4.

Accurate determinations of the specific heats of organic compounds in the solid, liquid and gaseous condition and at various temperatures will undoubtedly be of great service in establishing the character of the vibrations of the atoms and the nature of the forces controlling them. The available data at present are very meagre and unreliable.

Chemical Compounds Existing Only in the Solid State

From what has been said regarding the relation between primary and secondary valences in solid bodies, it would follow that in general the composition of a solid body should give us little or no information about the primary valences. Conversely, we should expect more compounds to exist in the solid state than we would be led to predict from the ordinary rules of valence.

When we consider that every atom (and every molecule for that matter) is surrounded by a field of electro-magnetic force, it appears probable that solids can be built up with almost any arrangement of atoms, provided the temperature is sufficiently low. If these arrangements of atoms are regular

---

[1] *Verh. deut. physik. Ges.* **15**, 969 (1913).

[2] *Phys. Rev.* **6**, 377 (1915).

[3] Nernst, *Theoretische Chemie*, 1903, p. 180.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

so as to constitute a space lattice, the resulting solid will have a definite and invariable chemical composition which can be represented by a chemical formula, and would, therefore, be recognized as a chemical compound. The arrangement of the atoms in such compounds would bear no more relationship to the primary valence of the atoms than does the arrangement of the carbon, oxygen and calcium atoms in a crystal of calcite. The formula representing a compound of this type would thus be totally unrelated to the valence of the atoms.

The reason that the composition of solid compounds is so often consistent with the ordinary valence rules, is probably that the compounds are formed from solutions or from gaseous phases. In liquids or gases there is naturally more opportunity for the primary valences to manifest themselves.

As a matter of fact there are vast members of chemical compounds which exist in the solid state only and among these compounds the absence of valence relations is very striking.

Tammann and his students have proven the existence of a hundred or more definite metallic compounds by their studies of alloys. Out of 100 such compounds only 26 have formulas which agree with the ordinary valence.[1] A few typical compounds are $AgMg_3$, AgMg, AuZn, Au_3Zn_5, Cu_3Al, CuAl, $CuAl_2$, Mg_4Al_3, AlSb, Zn_7Fe, Zn_3Fe, Al_5Fe_2, $NaZn_{12}$, $NaCd_5$, $NaHg_4$, $NiCd_5$, $AuSb_2$, etc. Tammann shows that definite compounds are never formed between metals which are closely related in the periodic system, such as Cu-Ag or Fe-Ni, although solid solutions or mixed crystals frequently form in these cases.

If we consider these metallic compounds from the viewpoint we have developed above, it is evident that the atoms are held together by secondary valence, as are for instance those in a copper crystal or a rock-salt crystal. The reason that they have a definite chemical composition is that the atoms are arranged in some form of regular lattice. For example, if, in a face centered cubic lattice such as that of a copper crystal, we should replace the corner atoms by atoms of an element A, and replace the atoms in the faces of the cubes by atoms B, then we should have a compound of the composition AB_3. Each atom A would be surrounded by twelve atoms B all equidistant. Each atom B, however, would have 4 atoms of A and 8 of B equidistant from it. Such a structure would reveal nothing as to the valency of the atoms. It is quite probable that the compound $AgMg_3$ has a structure of this kind.

If the atoms of the copper crystal we have considered should be replaced by atoms of two elements A and B in an irregular manner, then the resulting crystal would not have a definite chemical composition and would, therefore, not be recognized as a chemical compound, but would be con-

---

[1] Tammann, *Z. anorg. Chem.* **49**, 113 (1906) and **55**, 289 (1907).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

sidered a solid solution or mixed crystal. Yet there is no reason to assume that the forces holding the crystal together in one case are any different from those in the other.

If the two elements have combined together to form a chemical compound in one case, why not assume that the elements are equally combined in the mixed crystal? In the crystal of a pure metal we should also consider the atoms chemically combined with one another.

In mixed crystals or solid solutions, the atoms are evidently arranged in a haphazard manner according to the laws of probability, many different arrangements of atoms occurring side by side in the crystal. If the atoms of the two elements differ sufficiently in size or in their fields of force, then certain of these arrangements will be more stable than others. Thus, although at low temperatures almost any conceivable arrangement of atoms might be stable, it may be impossible to form mixed crystals by cooling a molten mass, because the atoms during the process of solidification have ample opportunity to arrange themselves in the most stable arrangements.

Thus the limitation in the number of compounds actually found is probably due to the restrictions imposed by our present methods of preparing these alloys by solidification from a melt, and is not an indication that such chemical compounds (or solid solutions) are not capable of existence in the solid condition.

Mineralogy also affords us an abundance of compounds which exist in the solid condition only and whose composition is not in accordance with the ordinary valence rules. The complex silicates are apparently built up of compounds of the first order (SiO_2, K_2O, Al_2O_3, H_2O, etc.) in much the same way that the metallic compounds are built up of the atoms of the metals. If we consider such typical compounds as $(K_2O)(Al_2O_3)(SiO_2)_6$; $(MgO)_3(SiO_2)_4(H_2O)$; $(MgO)(SiO_2)(_2H_2O)_2$, etc., it appears that the number of each of the groups (K_2O), (Al_2O_3), etc., which enter into the formula bears no relation to the valence of the elements. It is probable that in many cases each of the groups K_2O, Al_2O_3 really constitute group molecules and that these are held together in the crystal by secondary valence, just as the atoms of the metallic compounds are.

Solid solutions or mixed crystals are of even more frequent occurrence among minerals than among alloys, and similar considerations must apply in regard to their constitution.

In the field of inorganic chemistry, especially in that of complex salts so well covered by Werner and his students, the relative number of compounds that can exist in the gaseous condition is extremely small.

Practically all complex compounds decompose or dissociate when heated. Even sulfuric acid gives a vapor whose density indicates that it is completely dissociated into H_2O and SO_3. In fact the great majority of complex compounds do not even show a molecular weight in solution which cor-

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

responds to their composition in the solid state. For example, when alum $(K_2O.)(Al_2O_3)(SO_3)_4(H_2O)_{24}$ is dissolved in water it shows a "molecular weight" very much less than that corresponding to its formula. Crystals containing water of crystallization cannot be made to evaporate and still retain the combined water.

The number of complex compounds that be formed must be unlimited. If methods can be found for forming them at sufficiently low temperature, probably almost any conceivable arrangements of group molecules could be built up having definite chemical compositions. Or solid solutions consisting of almost any combination of atoms and molecules could theoretically be formed. We are only sharply restricted in the formation of compounds in the case of compounds of the first order. But there is no sharp limit to the compounds that may be formed by secondary valences.

So far we have considered only crystalline solid bodies. It is evident that atoms or group molecules could be arranged irregularly in space (not according to a regular space lattice). A solid body built up in this way would have the properties of an amorphous body or glass. There can be little reasonable doubt, but that the structure of glass is of this nature. Such a structure is naturally much more easily built up of group molecules than of atoms for the greater symmetry of the atom enables it to assume definite and regular positions with respect to its neighbors more readily than group molecules could do.

The nature of the forces acting between the atoms or group molecules in amorphous bodies cannot be essentially different from that in crystals. We should expect the union between adjacent atoms or molecules to be dependent upon exactly the same kind of chemical properties as those which determine the combination of the atoms or molecules to form complex compounds (secondary valence).

From the fact that glasses, when heated, change to the liquid state by a continuous process, we are led to conclude that the structure of a liquid does not differ from that of a glass in any essential respect except that in the liquid there is a certain mobility (entirely analogous to tautomerism). Therefore, even in a liquid we look upon every atom (or group molecule) as combined chemically (or adsorbed) to all the adjacent ones. The molecular weight is, therefore, a term that has very little significance in the case of a liquid. This theory of the structure of liquids will be developed in more detail in the second part of this paper.

Structure of the Surfaces of Solids

Unfortunately the study of crystals by the X-ray spectrum has not yet given us any direct knowledge of the structure of the surfaces of solids. From the point of view of the chemist, the structure of the surface must be

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of the utmost importance, for chemical reactions in which solids take part are practically always surface reactions.

Our knowledge of the surfaces of solids must, therefore, be derived from indirect sources.

Since the forces that hold the atoms of solids together are of the same kind as those that hold the atoms of complex chemical compounds, we have excellent reasons for believing that the forces decrease extremely rapidly as the distance between atoms increases. We may also draw this conclusion from the compressibility of solids.

The energy which must be expended in separating the atoms of a solid metal from each other is given by the latent heat of evaporation λ (per gram atom). We can also calculate the energy necessary to change the distance between atoms from the compressibility. By comparing this energy with the latent heat, we may estimate the distance through which atomic forces are effective.

Let K represent the coefficient of compressibility of an element having an atomic volume A/ϱ. We have good reasons for believing that the atoms of a solid are subject to forces that vary in proportion to the displacement of the atoms from their equilibrium positions.[1]

If we compress a unit volume of a solid so as to decrease its volume by the amount ΔV the work expended will be $(\Delta V)^2/2K$. If the body is subjected to tension in all directions (negative pressure) so as to *increase* its volume by the amount ΔV, the work expended will also be $(\Delta V)^2/2K$. This relation will hold accurately only for such small negative pressures that K remains constant. It is evident that as the atoms are being separated from each other, the attractive forces will at first increase in proportion to the displacement, then gradually more slowly, until finally the attractive force reaches a maximum. Beyond this distance the force rapidly decreases (probably according to about the inverse 4th or 5th power) to negligible values. It will be very instructive, however, to calculate on the assumption that K is constant, how far we need to pull the atoms apart before the work expended will equal the known latent heat of evaporation.

We readily obtain

$$(\Delta V_0)^2 = \frac{2\lambda K}{A/\varrho}.$$

---

[1] The specific heats and other properties of the heavier elements compel us to this view when the displacements are small. Richards has shown that the compressibility of the elements decreases gradually as the pressure is raised to very high values. This proves that the repulsive forces between atoms increase more rapidly than the displacement. It is well known that liquids can be subjected to negative pressures and have substantially the same coefficient of compressibility for negative as for positive pressures. Undoubtedly the coefficient K should increase considerably for very intense negative pressures. Nevertheless, the assumption of a constant value of K could hardly affect to order of magnitude *of the calculated* range of atomic forces.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

In this equation ΔV_0 represents the increase in volume which could cause an expenditure of energy equal to λ per gram atom. The volume is thus increased from 1 to $1+\Delta V_0$. The relative increase in the distance between the atoms is given by $\sqrt[3]{1+\Delta V_0}$. In Table I the data for several elements are given. According to Richards, tungsten is the least compressible and caesium the most compressible metal.

TABLE I

Metal	K C. G. S. units	λ ergs	A/ϱ	$\sqrt[3]{1+\Delta V_0}$	σ cm	$\Delta\sigma$ cm
W	0.28×10^{-12}	9.2×10^{12}	9.6	1.20	2.8×10^{-8}	0.57×10^{-8}
Pt	0.38×10^{-12}	5.4×10^{12}	9.1	1.19	2.78×10^{-8}	0.53×10^{-8}
Mo	0.46×10^{-12}	7.4×10^{12}	11.1	1.21	2.96×10^{-8}	0.62×10^{-8}
Hg	3.95×10^{-12}	0.58×10^{12}	14.8	1.16	3.26×10^{-8}	0.52×10^{-8}
Cs	61.0×10^{-12}	1.0×10^{12}	71.0	1.12	5.50×10^{-8}	0.66×10^{-8}

Thus, if the attractive forces between the atoms varied in proportion to the displacement, the expenditure of energy necessary to increase the distance between the atoms by 12% in case of caesium (or 21% in case of molybdenum) would be as great as that actually required to separate them to an infinite distance.

Actually, the attractive force can vary proportionally to the displacement only for displacements much less than 10% of the distance between atoms. However, the distance calculated by the above rough method is probably very close to that at which the *maximum attractive force* occurs. The work done in separating the atoms beyond this distance probably compensates for the decrease in attractive force before the maximum is reached.

From these considerations it seems safe to say that: *The attractive force between atoms reaches a maximum when the atoms are separated by distances* 10–30% *greater than the distance at which they are in stable equilibrium*[1]. Since the force varies with a high power of the distance, we may also conclude: *The attractive force becomes practically negligible when the distance between the centers of the atoms becomes twice as great as the distance at which the atoms are in equilibrium*[2].

It is interesing to note in Table I that the values of $\sqrt[3]{1+\Delta V_0}$ are largest for the elements of smallest atomic volume. This suggests that the increase in actual distance at which the attractive force becomes a maximum may be approximately the same for all the elements. In the sixth column are given

[1] Grüneisen (*Ann. Physik* **39**, 298 (1912)) by a mathematical development of a theory of monoatomic solids concludes that the average *amplitude of vibration* of the atoms in a solid at its melting point is 8.5% of the distance between the atoms.

[2] Probably the best evidence of the very limited range of atomic forces is that afforded by surface tension phenomena. This will be discussed in the second part of the paper.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the distances between the centers of the atoms calculated from the atomic volume on the assumption that the atoms are arranged according to a face-centered cubic lattice. The next column gives $\Delta\sigma$, the increase in this distance corresponding to the increase in volume represented by $1+\Delta V_0$. It is seen that the values of $\Delta\sigma$ are substantially constant so that we may conclude that: *The attractive forces between atoms increase to a maximum when the distance between the atoms is about* 0.6×10^{-8} *cm greater than the distance at which the attractive force is zero.*

We are now in a position to draw certain conclusions regarding the structure of the surfaces of crystals.

Let us consider a crystal such as calcite in which cleavage surfaces may be obtained. To break a crystal into two parts requires the expenditure of a certain amount of energy. Let γ be the *work* or *free energy* which must be expended in producing each square centimeter of cleavage surface. Thus if we have a crystal of one square centimeter in cross-section (parallel to cleavage face), γ will be one-half of the work required to separate the crystal into two parts. In general γ will decrease as the temperature rises. If we consider the mechanism of the formation of a cleavage surface, it is evident that as the atoms are pulled away from each other a certain amount of work will be done by the thermal agitations of the atoms. The atoms moving towards the receding surface are repelled by a gradually decreasing force so that they return from the receding surface with a velocity lower (on the average) than that with which they started out. Thus there must be a certain cooling effect accompanying the formation of a cleavage surface and this heat energy must result in a corresponding decrease in the free energy required to produce the surface. This reasoning is entirely analogous to that in the case of the mechanism of the adiabatic expansion of a gas.

Simple thermodynamical reasoning (see first chapter of Nernst's Theoretical Chemistry) shows that in the production of a cleavage surface the amount of energy contributed by the thermal agitation is equal to $-\mathrm{T}\,d\gamma/d\mathrm{T}$. If we add to this the free energy expended, we obtain, for the total energy involved in the formation of a unit surface, the expression

$$\gamma_0 = \gamma - \mathrm{T}\frac{d\gamma}{d\mathrm{T}}. \qquad (2)$$

This quantity γ_0 represents the total potential energy of the surface. Since we look upon atomic forces as electromagnetic in nature, the quantity γ_0 is a quantitative measure of the increase in the energy of the electromagnetic field surrounding the atoms, produced by the formation of the surface.

Just as we traced a relationship between the compressibility, the heat of vaporization and the range of atomic forces, we may derive a similar relationship between the elastic properties, surface energy and range of atomic forces. Unfortunately, however, few data on the surface energy of solids are available.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

There is every reason for believing that the range of atomic forces is of the same order of magnitude in all the states of matter. In forming a cleavage surface, therefore, it is probable[1] that the atoms pull part when the distance between adjacent atoms has been increased by about 0.6×10^{-8} cm.

When electrically charged or magnetized bodies are brought into proximity, they tend to move in such a way that the total energy of the electric or magnetic field becomes a minimum. For example, if we imagine a number of small horseshoe magnets to be placed in a box and shaken, we should expect on opening the box to find that the magnets had become attached to each other in pairs in such a way that in each pair the north pole of one is in contact with the south pole of the other. This arrangement would be a very stable one and would require a maximum amount of energy to break it up.

In a similar manner the atoms in the surface of a crystal must tend to arrange themselves so that the total energy in the field surrounding them will be a minimum[2]. In general, this will involve a shifting of the positions of the atoms with respect to one another. However, from the fact that energy is always required to separate a solid body into two parts we must conclude that the field energy associated with the surface atoms is always greater than that associated with a like number of atoms in the interior of the solid, notwithstanding the shifting of the positions of the atoms in the surface layer.

The smallness of the range of the atomic forces, compels us to conclude that in general the distances through which the surface atoms are shifted from their original positions in the solid, are small compared to the average distance between atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only.

The surface of a solid (or liquid), therefore, does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or "molecules" in the surface layer in such a way that the part of the molecule which has the weakest field around it actually forms the surface, while the more active parts of the molecule are drawn below the surface, and are then without effect on the surface tension except in so far as they crowd the surface atoms apart.

The above principle also seems to be related to the cleavage or crystal habits of solids. In a crystal built up of atoms arranged according to a face centered cubic lattice the number of atoms per sq. cm of crystal face is $5.56\times10^{15}\times V^{-2/3}$ for the 1:0:0 faces; $4.02\times10^{15}\times V^{-2/3}$ for the 1:1:0 faces and $6.57\times10^{15}\ V^{-2/3}$ for the 1:1:1 faces. Here V is the atomic volume. Thus the atoms are arranged more compactly in the octahedron faces than in any others.

For such faces the value of γ_0 should be a minimum. When platinum is slowly sublimed at high temperatures as, for instance, in the winding of an electric furnace, it crystallizes in the form of beautiful octahedra. The writer has observed similar crystals of tungsten.

On the other hand, in the simple cubic lattice the most compact arrangement of the surface atoms occurs in the 1:0:0 faces. Crystals of the alkali halides have cubic cleavage and usually crystallize as cubes and the *atoms* in these crystals are spaced according to a simple cubic lattice.

[1] Further evidence in support of this statement will be given in the second part of this paper.

[2] In the second part of this paper it will be shown that this principle is of great importance in connection with surface tension phenomena. The group molecules in liquids arrange

Digitized by Google Original from UNIVERSITY OF MICHIGAN

cules", in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. In a sense, the rearrangement of the atoms in the surface layer causes this layer to assume the character of a transition layer, but the density of the packing of the atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of the space. Additional evidence in favor of this view will be given in the remainder of this paper.

The surface of a crystal must then consist of an arrangement of atoms as definite as that existing in the interior of the crystal, although slightly different from the latter. The surface must thus be looked upon as a sort of checker board containing a definite number of atoms, of definite kinds arranged in a *plane* lattice formation. The space between and immediately above (away from the interior) these atoms is surrounded by a field of electromagnetic force more intense than that between the atoms inside the crystal.

There are good reasons for believing that the intensity of this surface field of force is substantially independent of the temperature. The energy in the surface field is measured by γ_0. (Equation 2.) Now the work done, during the formation of a fresh surface by the thermal agitation of the molecules (namely, $-\mathrm{T}\, d\gamma/d\mathrm{T}$), should be approximately proportional to the temperature. Therefore, $d\gamma/d\mathrm{T}$, should be independent of the temperature. Thus we may place

$$\gamma = a - b\mathrm{T} \tag{3}$$

where a and b are constants. Combining this with (2) we find $\gamma_0 = a$. In other words, γ_0, the total energy of the electromagnetic surface field should be independent of the temperature.

In the case of liquids, the free energy necessary for the formation of unit surface is called the surface tension. By analogy we would be justified in calling γ the surface tension of the solid. However, on the whole, it seems preferable with both solids and liquids to refer to the quantity γ as the *free surface energy* and γ_0 as the *total surface energy*.

Sublimation of Solids

Sublimation involves two processes; evaporation and condensation. Condensation being in some ways the simpler of the two will be considered first.

Condensation of Vapors.—When a crystal is in contact with its own saturated vapor the vapor must be continually condensing on the solid while the solid is evaporating at an equal rate. The rate at which the molecules of the vapor come into contact with the surface of the solid is given by the equation

$$m = \sqrt{\frac{\mathrm{M}}{2\pi\mathrm{RT}}}\, p, \tag{4}$$

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

where M is the molecular weight of the vapor, R is the gas constant, p is the pressure of the vapor and m is the rate at which the gas molecules strike against the surface, expressed in grams of vapor per sq. cm per second[1].

When a molecule of vapor strikes against the solid surface one of two things may happen. The molecule may be *reflected* from the surface, in other words, may rebound elastically, or it may *condense* on the surface, that is, it may be held by attractive forces in such a way that it forms at least temporarily a part of the solid body. It is of importance to know approximately what fraction of the molecules striking the surface are reflected.

In the kinetic theory of gases it has almost universally been assumed that molecules are perfectly elastic. This assumption has become so much a habit of thought that nearly everyone who has applied the kinetic theory to liquids and solids has taken it for granted that the collision between gases and surfaces of solids or liquids are also elastic[2].

We have seen, however, from a consideration of the heat conductivity of solids that the time of relaxation of the atoms is usually small compared to the time necessary for the atom to complete a single oscillation. This means that before an atom can be displaced a perceptible distance the energy causing the displacement has been dissipated among all the adjacent atoms. From this fact it appears that the collisions of molecules against solid bodies must in general be almost wholly inelastic.

In a recent paper in the *Physical Review*[3] the writer has discussed this question very fully, and gives abundant evidence both experimental and theoretical, for the inelasticity of the collisions between gas molecules and solid surfaces. There are apparently some cases in which a moderate amount of real reflection does occur, but these cases must be looked upon as the exception rather than the rule.

According to this viewpoint the mechanism of the condensation of a vapor on a solid is as follows:

In the vapor surrounding the solid, the average distance which the molecules travel between collisions (the mean free path) is of the order of magnitude of 10^{-5} cm if the pressure is atmospheric, while it is correspondingly greater if the pressure is less. When a vapor molecule approaching the surface comes within a distance of about 2×10^{-8} cm of the surface layer of atoms it begins to be acted upon by the electromagnetic field close to the surface. The vapor

---

[1] This equation is a simple modification of the equation giving the rate of effusion of gases through small openings (Meyer's *Kinetic Theory of Gases*, German edition, 1899, p. 82). Its derivation was given by the writer in an article in the *Phys. Rev.* **2**, 331 (1913). The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasized. See for example Langmuir, *J. Am. Chem. Soc.* **37**, 1144 (1915).

[2] N. T. Bacon (*J. Phys. Chem.* **17**, 762 (1913)) suggests that molecules are not elastic, and in this way explains qualitatively the phenomena of adsorption and catalytic action.

[3] *Phys. Rev.* **8**, 149 (1916).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

molecule thus experiences a force attracting it towards the surface. As it moves closer to the surface the attractive force rapidly increases and soon reaches a maximum intensity. The attractive force then rapidly decreases, and falls to zero when the molecule has traveled a distance only about 0.6×10^{-8} cm beyond the point at which the force was a maximum. The point at which the force falls to zero may be regarded as an equilibrium position. When the molecule reaches this position its kinetic energy will be very high for a relatively large amount of work has been done upon it by the attractive forces. It will, therefore, not remain in the equilibrium position, but will move still closer to the atoms of the solid, and will thus enter a region in which it is subjected to very strong and rapidly increasing repulsive forces. If the molecule had lost no energy to adjacent atoms it would probably travel a distance $0.2—0.3\times10^{-8}$ cm against these repulsive forces before being brought to rest. It would then pass again through the equilibrium position and finally out through the region of attractive forces, and might thus again escape from the surface forces, in other words, be reflected.

But the improbability of such a reflection is evident when we consider the ease with which energy is dissipated to adjacent atoms. This energy loss occurs in two ways. In the first place, when the molecule is approaching the surface, the attractive force is exerted by *several atoms* on the surface. These atoms are thus all accelerated towards the incident molecule. A little later when the molecule is in the region of repulsive forces, these forces will be exerted principally by a *single atom* of the solid. The energy used in accelerating the surface atoms can, therefore, only partially be delivered back to the incident molecule. This dissipation in energy, even if only relatively small, will usually make it impossible for the molecule to pass out through the region of attractive forces.

The second kind of loss of energy, which is probably the more important, is that which causes the remarkably small time of relaxation in solid bodies. We have seen that in the interior of crystals the time taken for adjacent atoms to reach thermal equilibrium with each other is of the order of 10^{-16} seconds. The duration of a collision between a molecule and a surface (that is, the time between successive passages through the region of maximum attractive force) must be of the order of 10^{-13} seconds. Thus in general, the energy delivered to the incident molecule by the attractive forces, is practically wholly dissipated to the adjacent atoms by the time the molecule first reaches the equilibrium position. It, therefore, has not sufficient kinetic energy to enable it to penetrate far into the region of repulsive forces, and certainly not sufficient to allow it to work against the attractive forces and thus escape from the surface.

The condensation of a vapor on a solid surface thus takes place independently of the temperature of the surface[1].

---

[1] It must of course be remembered that what we ordinarily observe during the condensation of a vapor is the difference between the rate of condensation and the rate of evaporation.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

This is especially evident when we consider that the intensity of the field of force close to the surface, as measured by the total surface energy γ_0, is itself independent of the temperature. The rate of evaporation on the other hand varies extremely rapidly with the temperature.

If practically every molecule of vapor which strikes against the surface of the solid condenses, it is not at first evident how the molecules, especially if they are complex, are able to arrange themselves to form a crystalline mass. In analyzing the mechanism of condensation we must distinguish two extreme sets of conditions that may occur. These may be termed *irreversible* and *reversible* sublimation.

By *irreversible* sublimation I mean the type which occurs for instance when a tungsten filament is heated to a high temperature in a well evacuated bulb. Under these conditions there can be no equilibrium, for the bulb is at a temperature thousands of degrees lower than that at which the vapor can be produced. The vapor is thus enormously superheated with respect to the surface on which it condenses. Such conditions as this can only be realized in practice when the vapor is at very low pressure, for, otherwise, the amount of vapor condensed per unit area per second would be so great that the heat liberated by the condensation could not be removed rapidly enough to maintain a low temperature on the condensing surface.

By the term *reversible* sublimation we may designate that which takes place for example, when iodine or naphthalene is sublimed slowly at ordinary temperatures.

In this case we are dealing with small differences of temperature, and we shall see that under these conditions condensation and evaporation are going on simultaneously at nearly equal rates over every portion of the surface where condensation occurs.

The mechanisms of reversible and of irreversible sublimation are in some ways quite different, and from the experimental side the phenomena show marked distinctions.

In the irreversible sublimation the vapor molecules remain where they first strike the surface, since they can neither be reflected nor re-evaporated. The deposit formed by the condensed vapor is, therefore, homogeneous (when gaseous impurities are absent) and is of uniform thickness. If the temperature of the surface on which condensation occurs is sufficiently low, the deposit will be wholly noncrystalline, since the atoms or molecules become rigidly fixed in position when they strike the surface and thus have no opportunity to arrange themselves as in a crystal. With the condensing surface at higher temperatures, however, a sintering or crystallizing process may go on within the deposit even when the temperature is below that at which perceptible vaporization occurs.

By means of this irreversible sublimation it is possible to obtain any volatile body in a noncrystalline form.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

In the case of reversible sublimation the deposit formed from the condensed vapor is ordinarily very crystalline, frequently consisting of groups of separate crystals. In the formation of these crystals every molecule of vapor which strikes the surface condenses just as in the case of irreversible condensation, but most of these molecules re-evaporate again. The tendency of different molecules to re-evaporate will depend entirely on how firmly they are held by the atoms of the crystal. Thus the molecules which strike the surface in such a way as to form a continuation of the space lattice already present, will evaporate much less frequently than molecules which are not in positions where they can fit in with the crystal structure. The continual evaporation and condensation going on over the whole surface of the crystal allows the atoms to arrange themselves in the most stable positions. The smaller the differences in temperature and the more nearly equal the rates of condensation and evaporation, the more perfect will be the development of the crystals.

Evaporation of Solids.—We have seen that the condensation of vapors on a solid body takes place at a rate which is practically independent of the temperature. The rate of evaporation, however, increases rapidly with temperature.

Since evaporation and condensation are in general thermodynamically reversible phenomena, ***the mechanism of evaporation must be the exact reverse of that of condensation***, even down to the smallest detail.

In the condensation of a monatomic vapor such as that of a metal, each atom as it approaches the surface comes into a region in which it is attracted. It is thus accelerated, but it gives up its newly acquired energy to adjacent atoms nearly as fast as it receives it. It soon reaches a region of repulsive forces, and is then brought to a stop. It then continues to move about an equilibrium position with an irregular motion due to thermal agitation.

Conversely in the evaporation of an atom of a metal the atom must acquire energy from adjacent ones and thus be accelerated outward. As it moves it must receive successive increments of energy from its neighbors until finally it passes out of the region of attractive forces. From the smallness of the time of relaxation we are thus compelled to believe that an atom only escapes when it thus receives a very large number of successive impulses from the adjacent atoms.

The very small probability of such a sequence of favorable impulses is the reason that so few atoms evaporate at lower temperatures.

We may picture to ourselves the mechanism of evaporation by imagining a large number of heavy balls suspended (according to a two-dimensional lattice) from a ceiling by steel springs. Each ball is to be coupled to each of its neighbors by springs under tension. If some of the balls are set in motion the energy will be rapidly propagated to the others so they will all be in a state of agitation. To properly imitate the structure of a solid the coupling between the balls should be so stiff that the total energy of one ball can be transmitted to its

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

neighbors in a very small fraction of the time required for a single oscillation.

When all the balls have been in motion long enough for a steady state to have been reached the velocities will be distributed among them according to the probability laws, in other words, according to Maxwell's distribution law.

If the springs are of brittle wire so that they snap when elongated more than a certain amount, then from time to time balls which have acquired an unusually large downward displacement will break their springs and escape. This will be quite analogous to evaporation.

The rate of evaporation of a solid is thus determined by the number of surface atoms per second which reach a certain critical condition. By means of Maxwell's distribution law it can thus be readily shown[1] that the rate of evaporation should increase with the temperature according to an equation of the form

$$m = \mathrm{A}\sqrt{\mathrm{T}}e^{-\lambda/RT} \tag{5}$$

where λ is the internal latent heat of evaporation per gram atom, and A is a constant whose value will depend primarily on the degree of coupling between adjacent atoms.

In the study of the disintegration of radioactive substances it has been customary to speak of the life or period of the atom. In a similar way we may calculate the "life" of an atom on the surface of an evaporating solid.

The number of atoms evaporating per second per sq. cm of surface will be $\mathrm{N}m/\mathrm{M}$ where N is the Avogadro constant and M is the atomic weight of the substance. If N_0 is the total number of atoms per sq. cm of surface then t, the average life of an atom on the surface will be

$$t = \frac{\mathrm{N}_0\mathrm{M}}{\mathrm{N}m}. \tag{6}$$

The "half period," that is, the time which must elapse before half of any selected lot of atoms will have evaporated, is equal to

$$t_{1/2} = 0.693\,\frac{\mathrm{N}_0\mathrm{M}}{\mathrm{N}m}. \tag{7}$$

We have just seen that the constant A in Equation (5) is dependent on the coupling between the atoms. The time of relaxation of the atoms is also a measure

---

[1] Richardson (*Phil. Trans.* **201**, 516 (1903)) calculated in this way the rate of evaporation of electrons from heated metals (thermionic emission). The derivation of Equation 5 is also given by the writer (*J. Am. Chem. Soc.* **35**, 122 (1913)) in connection with a study of the reaction between oxygen and tungsten at high temperatures. It was also pointed out that this equation is substantially equivalent to Arrhenius' equation for the temperature coefficient of reaction velocity.

The significance of Maxwell's distribution law in relation to the kinetics of chemical reactions has been very fully treated in a recent paper by R. Marcellin (*Annales de Physique* **3**, 185 (1915)).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

of this coupling. It should thus be possible to estimate the time of relaxation from the rate of evaporation, and it will be of interest to see how the result calculated in this way compares with that found from the heat conductivity.

We see from Equation (5) that the rate of evaporation, m, depends on the latent heat of evaporation. If we substitute $\lambda = 0$ in Equation (5) we obtain a hypothetical value of m_0 (let this be m), that represents the rate of evaporation which would occur if attractive forces did not prevent the escape of atoms from the surface. Thus we obtain from (5)

$$\frac{m}{m_0} = e^{-\lambda/RT}. \tag{8}$$

By Equation 6 the average life of an atom on the surface of a solid evaporating at the rate m_0, is

$$t_0 = \frac{N_0 M}{N m_0}. \tag{9}$$

Eliminate m_0 between (8) and (9).

$$t_0 = \frac{N_0 M}{N m} e^{-\lambda/RT}. \tag{10}$$

Or from (5)

$$t_0 = \frac{N_0 M}{NA\sqrt{T}}. \tag{11}$$

The quantity t_0 thus represents the average length of time an atom would remain on the surface if there were no attractive forces to hold it. Now the "time of relaxation" has been defined as the time required for an atom to give up all but $1/e^{1c}$ of its excess energy to adjacent atoms. It is evident that the time required for an atom at rest to be set in motion will also be measured by the time of relaxation. Thus t_0 should be of the same order of magnitude as the time of relaxation, and probably only differs from it by some constant factor not very far from unity.

The rates of evaporation of tungsten[1] platinum and molybdenum[2] in a very high vacuum, have been measured by Mr. G. M. J. Mackay and the writer. The values of t_0, calculated from these data by Equation 10 are given in Table II.

TABLE II

	W	M_0	Pt
N_0	1.46×10^{15}	1.32×10^{15}	1.51×10^{15}
t_0 at 300°K	3.4×10^{-19}	3.5×10^{-20}	1.1×10^{-16}
t_0 at 2000°K	5.2×10^{-16}	1.0×10^{-16}	3.0×10^{-15}
t_r by Equation I	1.3×10^{-15}	.....	2.3×10^{-15}

[1] *Phys. Rev.* **2**, 329 (1913).

[2] *Ibid.* **4**, 377 (1914).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

For comparison, the "times of relaxation" t_r calculated by Equation (1) are given in the last line. It will be remembered that Equation (1) gives too high a value for t_r because it was assumed in its derivation that an atom could take up energy only from atoms in one given direction. It is seen that the order of magnitude of t_r is not very different from that of t_r. We must not expect any very good agreement between t_0 and t_r because of the very great effect of slight errors in λ on the value of t_0 calculated by Equation (10). Thus if λ is taken one per cent too large the value of t_0 will be 20 times too small. On the whole, therefore, we may conclude that the values of t_0 calculated as above, furnish confirmatory evidence that the time of relaxation of the atoms in solids is hundreds if not thousands of times smaller than the "natural period" of atomic vibrations.

So far we have considered the evaporation of solids which give monatomic vapors. When a crystal such as sodium chloride evaporates the atoms must group themselves together in pairs *before* they escape from the surface forces.

The latent heat of evaporation does not correspond to the energy required to separate the atoms from each other, but only to the energy needed to separate one group of atoms from other similar groups. This makes it appear that evaporation in these cases is the result of a tautomeric change taking place among the surface atoms. Thus in the case of solid sodium chloride the sodium atoms are ordinarily held to the adjacent chlorine atoms by secondary valence. If, however, a tautomeric change occurs by which a pair of adjacent chlorine and sodium atoms becomes attached to each other by *primary* valences, then this pair will be held to the surface by much weaker forces than those holding other atoms not so combined. The pairs held by primary valences may thus be enabled to evaporate from the surface. We should not assume, however, that every pair of atoms so combined, or even the majority of them, will evaporate, for if we do, it would follow that only a very small fraction of molecules of salt vapor striking a surface would condense. It is more likely that the tautomeric changes take place with high frequency, but that the time during which a pair of atoms exists consecutively in the tautomeric form is comparable with the time of relaxation, that is, of the order of 10^{-17} seconds. Now the time required for an atom or a group of atoms to move out of the region of attractive forces (a distance of about 10^{-8} cm) must be *at least* 10^{-14} seconds, since molecular velocities are always less than 10^{6} cm per second. We are thus led to believe that a sodium chloride molecule only evaporates when the tautomeric change occurs at a moment when the atoms are already displaced from their equilibrium positions to an unusual degree.

The evaporation of compound substances of the polar type thus involves rather complicated chemical changes in which the atoms rearrange themselves according to their primary valences. This conception of the mechanism of evaporation receives support from the fact that so few complex polar compounds or molecular compounds can be volatilized without dissociation. Thus nearly

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

all inorganic salts except those which are compounds of the first order (halide salts for instance) are decomposed or dissociate on heating. Crystals containing water of crystallization can never be distilled with their water of crystallization. Even compounds like sulfuric acid give vapors which are dissociated.

Nonpolar compounds, such as most organic substances, usually contain fixed molecules which, even in the solid condition, are held together by primary valences, the secondary valences merely serving to hold the fixed molecules together. In this case evaporation involves only a breaking of the secondary valence forces so that it becomes quite similar to the evaporation of metals or other substances giving monatomic vapors.

Relation between Condensation and Evaporation.— When a solid is in equilibrium with its own vapor, condensation and evaporation are occurring simultaneously at equal rates. We have seen that we are justified, in the majority of cases, in considering that all the molecules of vapor which strike against the surface condense (are not reflected). Now the rate at which the molecules strike the surface is given by Equation (4)

$$m = \sqrt{\frac{M}{2\pi RT}}\, p. \qquad (4)$$

Since all of the molecules condense, and since the rate of evaporation must be equal to the rate of condensation, we may use this same equation to calculate the rate of evaporation, m, in terms of the pressure p, of the saturated vapor. If the condensation and evaporation go on independently of one another, then Equation 4 should give a means of calculating the rate at which a solid evaporates into a perfect vacuum. Or conversely if we determine the rate of evaporation of a solid in a high vacuum we can calculate the vapor pressure by the above equation[1].

This theoretical relation between the rate of evaporation and vapor pressure was first obtained by Hertz[2]. Hertz himself and others who have used the equation have not considered that the reflectivity is negligible and hence looked upon the calculated value of m as being greater than the true rate of evaporation.

R. Marcellin[3] has recently attempted to measure the maximum rate of evaporation of naphthalene, nitrobenzene and iodine, in a vacuum, and compares his results with those calculated by Equation (4). He concludes that at 40° only about one molecule out of 20 striking the surface condenses, while at 70° about one out of five condenses. That is, the reflectivity decreases rapidly at

---

[1] The writter, together with Mr. G. M. J. Mackay, has used this method for measuring the vapor pressures of the metals tungsten, platinum, molybdenum, iron, nickel, copper and silver, and the results have been, or will be, published in the *Physical Review*. The reasons which justify the assumption that the reflectivity is negligible, are given in detail in a recent article (*Phys. Rev.* **8**, 149 (1916)).

[2] *Ann. Physik* **17**, 177 (1882).

[3] *Annales de Physique* **3**, 185 (1915).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

higher temperatures. It should be noted on the other hand that R. W. Wood[1] finds no reflection of mercury atoms from a surface at very low temperatures but concludes that the atoms are all reflected at higher temperatures.

Marcellin measured the rates of evaporation of substances in capillary tubes. By plotting the rate of evaporation against the length of the tube through which the vapor had to pass, he *extrapolated* back to zero length of tube, and expected in this way to find the rate of evaporation in a perfect vacuum. When we consider that this extrapolation was carried out over a length of tube at least eight times the diameter of the tube, we realize how very few of the molecules evaporating from the surface could have escaped, from the end of the tube. The great majority of them must have struck the walls of the tube and thus have been afforded an opportunity of returning back onto the surface. Measurements of this sort, to have any value, must be made so that molecules evaporating from the surface may move off in straight lines without meeting any obstruction until they strike the cooled surface on which they permanently condense.

If Marcellin had plotted the reciprocal of the speed of evaporation (which should be a linear function of the length of the tube) instead of the speed itself, it would have been apparent, first that the observed rates were much lower than the true maximum rates, and second, that even with the small capillaries he used he did not succed in keeping the temperature of the evaporating surface up to that of the bath surrounding the tube. Therefore, it appears that Marcellin's experiments are entirely consistent with the view that the true rate of evaporation is accurately given by Equation 4.

The writer has also shown[2] that Wood's experiments may equally well be explained by assuming, instead of a reflection of mercury atoms, at the higher temperatures, a condensation followed by evaporation.

For the case of a clean surface of liquid mercury evaporating into a good vacuum Knudsen has recently[3] proved that Equation 4 gives the actual rate of evaporation.

Wood makes the statement that atoms of mercury which are "diffusely reflected" (or according to our theory, condensed and re-evaporated) from a surface, do not seem to be distributed quite according to Lambert's cosine law, but there seem to be too few atoms leaving the surface in directions nearly parallel to the surface. Now if evaporation and condensation can go on simultaneously, although independently, it must follow, according to Maxwell, that the number of atoms leaving the surface in different directions must be proportional to the projected area in that direction (Lambert's cosine law).

---

[1] *Phil. Mag.* **30**, 300 (1915).

[2] *Phys. Rev., loc. cit.*

[3] *Ann. Phys.* **47**, 697 (1915).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Observations on the evaporation of metals in high vacuum have convinced the writer that Lambert's cosine law does hold accurately for evaporation, and the Wood's conclusion is incorrect.

Wood drew his conclusions from the *apparent* sudden decrease in the thickness of a film of metal deposited on glass, in the region close to the plane of the surface from which "reflection" took place. In the writer's experience, this sudden decrease which he has often observed, and which certainly seems very real, is only apparent. It is due to the fact that, although the *thickness* of the film varies *linearly* with the distance from the plane of the surface, the *light absorption* varies *exponentially*.

Kaye and Ewen[1] have reported that at pressures of a few mm of gas, the sublimation from heated metals (Fe, W, Cu, Ag or Ir) appear to consist of two parts, one of which, diffuses like a gas, but the other, often the larger part, is projected in straight lines in a direction perpendicular to the surface at which it originates. In the experience of the writer such effects are due to convection currents (which often produce very freakish effects at pressures of a few mm) or to electric discharges through the gas. They are usually enormously stimulated by the presence of traces of moisture. In a thoroughly dry gas or in a good vacuum, and in the absence of electric discharges, the evaporation of heated metals takes place without any evidences of such "projection" of particles in definite directions. Of course in a really good vacuum the atoms leaving the heated surface, travel in perfectly straight lines until they strike an obstacle, and in this way "shadows" of interposed objects may be obtained. But this projection of particles takes place according to Lambert's cosine law and is in full accord with the ordinary conceptions of the kinetic theory.

We have assumed so far that evaporation and condensation can go on simultaneously without influencing each other. For example, in calculating by Equation (4) the rate of evaporation in a vacuum from the pressure of the saturated vapor, we had to assume that the true rate of evaporation in presence of saturated vapor is the same as that in vacuum, in other words, that the condensation of the vapor has no effect on the rate of evaporation.

There are, however, reasons which might lead us to expect a difference in the rate of evaporation in presence of and in the absence of vapor.

In the first place, when a vapor atom or molecule condenses on a surface an amount of energy corresponding to the latent heat of evaporation must be liberated, and must result in a local rise of temperature. It would seem that this might cause the evaporation of an adjacent atom which would otherwise not evaporate. Thus the condensation of vapor might stimulate the evaporation. This would be equivalent in many ways to a reflection of vapor molecules from the surface.

---

[1] *Proc. Roy. Soc.* (A) **80**, 58 (1914).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

The following considerations make it very improbable that condensation has any such effect on evaporation. The "average life" of an atom on a surface may be readily calculated from Equations (4) and (6). The life will be inversely proportional to the vapor pressure, and will be proportional to $\sqrt{MT}$. If we choose $M = 25$, $T = 400$ and $p =$ one megabar (atmospheric pressure) and assume that $N_0 = 10^{15}$ atoms per sq. cm we thus calculate that the life of an atom on the surface would be 3.8×10^{-9} seconds. In the evaporation of substances in vacuum the equilibrium pressure would always be extremely small compared to one megabar, so that the life of the atoms on the surface would be much more than 10^{-8} seconds. Now the time taken by an atom to receive or give up its energy to adjacent atoms is of the order of 10^{-17} seconds, or about 10^{+9} times less than the life of the atom on the surface. These figures show that the critical conditions necessary to cause the evaporation of an atom are of relatively rare occurrence. The chance is negligibly small, therefore, that an atom condensing on the surface will be able to give up its energy to an adjacent atom at a moment when the latter is nearly in its critical condition.

These considerations make it appear probable that the energy liberated by the condensation of vapor is totally without influence on the mechanism of evaporation.

There is, however, another kind of effect by which condensation may, and probably does, influence the rate of evaporation. Let us consider for example solid naphthalene in contact with its saturated vapor. When a molecule of naphthalene vapor strikes against the surface of the crystalline substance it undoubtedly condenses in the position in which it strikes. The chances are small that this position will be one in which the molecule forms a continuation of the space lattice of the crystal. If the temperature is sufficiently high the molecule may, by a sort of sintering process, readjust its position in conformity with the underlying group of molecules. But at lower temperatures this readjustment will often be impossible.

Such irregularly placed molecules will tend to evaporate from the surface more rapidly than those in the regular lattice positions.

We have already seen that this greater rate of evaporation manifests itself in the tendency for larger and more perfect crystals to be formed, as the sublimation of a substance is made more nearly reversible.

Since the rate of evaporation of the irregularly placed molecules must be finite, it follows that the surface must be more or less completely covered by such molecules. In other words, the surface of a crystalline solid in equilibrium with its saturated vapor may be covered by a layer of irregularly placed molecules, in other words, there may be an amorphous surface film.

The extent to which the surface is covered by such a film will depend upon the ease with which the molecules rearrange themselves, and also upon

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the relative rates of evaporation of the regularly and irregularly placed molecules.

It is of interest to consider the evaporation and condensation of a crystal of naphthalene under various conditions:

I. *Irreversible Condensation.*—If a stream of naphthalene vapor is admitted at low pressure into a well exhausted bulb immersed in liquid air, we should expect that all the molecules would condense in the positions in which they first strike the cooled bulb. The condensed material should then be wholly amorphous, both on its surface and in its interior.

2. *Irreversible Evaporation.*—If a naphthalene crystal is suspended in an exhausted bulb and the latter is immersed into liquid air, the naphtalene crystal will evaporate irreversibly, since no molecules of naphthalene will return from the surface of the bulb. In this case there will be no amorphous surface layer on the crystal.

3. *Reversible Evaporation or Condensation.*—If a naphthalene crystal is placed in one arm of an inverted and exhausted U-tube and the other arm is maintained at a very slightly lower temperature, the naphthalene will slowly sublime from one arm to the other, and form crystals in the cooler arm. These crystals as well as the one in the warmer arm will have amorphous surface layers.

If we calculate the rate of evaporation from the pressure of the saturated vapor by Equation (4) we obtain a value which corresponds to the rate of evaporation from the amorphous surface layer, and not from the true crystalline surface. Therefore, the rate of evaporation of a crystal in a good vacuum (Case 2, Irreversible Evaporation) should be lower than that calculated from the vapor pressure, notwithstanding the fact that no reflection of molecules from the surface takes place.

It is probable that in the great majority of cases, especially with substances such as metals which give monatomic vapors, that this effect is entirely negligible, because of the great ease with which the atoms can arrange themselves on the surface.[1]

Even with substances having molecules as complicated as that of naphthalene it seems improbable that the difference between the rates of evaporation of crystalline and amorphous surfaces would be great enough

[1] According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapor, must take place to the same extent, but in the reverse direction, in the evaporation of the substance. Thus if molecules rearrange themselves into regular positions, an equal number of molecules must be continually leaving regular positions to assume irregular positions. This leads to the conclusion that even with substances which give monatomic vapors, the surface must in part be amorphous. However, an amorphous structure due to this cause will be present to the same extent when the evaporation is irreversible as it is in the case of reversible evaporation. Therefore no error is made in calculating the rate of evaporation in a vacuum from the vapor pressure, according to Equation (4).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

to very seriously affect the validity of Equation (4), when applied to the calculation of the rate of evaporation in a vacuum. Accurate experimental determinations of the rates of evaporation of complex organic compounds in high vacuum should prove of great interest.

There are cases, however, where we may expect very radical differences between the true rates of evaporation *in vacuo* and the rate calculated from the vapor pressure by Equation (4).

Red phosphorus should furnish an example of this sort. The transformation of yellow into red phosphorus takes place very much more slowly than the rate at which molecules of phosphorus vapor strike against a surface of red phosphorus. Therefore, the molecules of phosphorus vapor which impinge against the surface and condense, must evaporate again without having been in the condition of red phosphorus.

The surface of the red phosphorus is, therefore, covered, at least in part, by a layer of fixed molecules which constitute an adsorbed film of yellow phosphorus. The rate of evaporation calculated by Equation (4) corresponds to the evaporation from this adsorbed film of yellow phosphorus plus that from the uncovered portion of the surface of red phosphorus. On the other hand if the red phosphorus is placed in a good vacuum the adsorbed film of yellow phosphorus will distill off and the observed rate of evaporation will correspond to the rate of conversion of red into yellow phosphorus. This rate will be very much less than that calculated from the equilibrium pressure.

It is thus probable in the case of red phosphorus that the equilibrium pressure is not a true vapor pressure in the ordinary sense, but is rather to be regarded as a dissociation pressure.

The rate of evaporation of ammonium chloride in a vacuum, both in the presence of and in the absence of traces of moisture, should throw a very interesting light upon the mechanism of the evaporation or dissociation[1] of this substance.

The Dissociation of Solids and the Kinetic Interpretation on the Phase Rule

Sometime ago it was pointed out to the writer by Mr. R. E. Wilson that a difficulty arises in the application of the kinetic theory to the dissociation of a substance such as calcium carbonate.

We may assume that in the equilibrium between calcium carbonate, calcium oxide and carbon dioxide two opposing reactions are taking place at equal rates. Off-hand, the most natural assumption in regard to these reactions would seem to be that the rate at which carbon dioxide is converted into carbonate is proportional to the pressure p of carbon dioxide and to the faction θ_1 of the surface which is covered by CaO. On the other hand

[1] See papers by Abegg and Johnson, *Z. physik. Chem.* **61**, 455 and 457 (1908); Scheffer, *Proc. Akad. Wetenschappen Amsterdam* **18**, 446 (1915).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the rate of dissociation of the carbonate would be proportional to the faction θ_2 of the surface covered by $CaCO_3$.

If we equate these two rates we obtain for equilibrium

$$p\theta_1 = K\theta_2 \qquad (12)$$

where K is the equilibrium constant. This equation indicates that the pressure of the CO_2 should depend on the ratio between θ_2 and θ_1; in other words it should depend on the relative proportions of the CaO and $CaCO_3$. This is contrary to fact. Evidently, therefore, we have made wrong assumptions regarding the mechanism of the reaction.

If we examine Equation (12) in the light of the Phase Rule we see that it would fit the facts well if there were a single solid phase of variable composition instead of two phases of constant composition. It would apply for instance to the dissociation of ferric oxide recently studied by Sosman and Hostetter[1] who found a "continuous series of solid solutions from Fe_2O_3 over to a point very near Fe_3O_4 if not over the entire range to Fe_3O_4."

Furthermore, when we analyze the assumptions made in the derivation of Equation 12 we readily see that they imply a solid solution phase. Thus if the rate of dissociation of $CaCO_3$ were proportional to the fraction of the surface covered by $CaCO_3$ it is evident that the surface would soon consist of CaO and $CaCO_3$ molecules distributed haphazard over the surface. This is exactly the kind of surface we should expect a solid solution to have.

The assumptions made above evidently are not consistent with the existence of separate phases of constant composition.

The Phase Rule, however, indicates that in the dissociation of calcium carbonate two solid phases, CaO and $CaCO_3$, are present together. In order that $CaCO_3$ may dissociate and form a phase of CaO (instead of a solid solution) it is *necessary that the reaction shall occur only at the boundary between two phases.*

Now the CaO phase is generally so porous that CO_2 readily diffuses through it. We are then forced to conclude that the CO_2 in passing through the CaO does not react until it reaches the boundary of the $CaCO_3$ phase. In a sense, therefore, calcium carbonate must be looked upon as a catalyst for the reaction between calcium oxide and carbon dioxide.

From the kinetic point of view this must mean that carbon dioxide molecules are only absorbed to form calcium carbonate when by so doing they form a continuation of a calcium carbonate crystal already present.

It will be remembered that in the calcite crystal each carbon atom is surrounded by three systematically placed oxygen atoms. By examining a model of such a crystal it is readily seen that in the cleavage surfaces two of the oxygen atoms are probably close to the surface, while the third lies well

[1] *J. Am. Chem. Soc.* **38**, 807 (1916).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

under the surface. In the readjustment of the positions of the surface atoms which must occur when a cleavage surface is found, the atoms must tend to assume positions in which the forces between the atoms are balanced against one another. Such an arrangement may have a considerable degree of stability

If we imagine one of the carbon atoms, with the pair of oxygen atoms adjacent to it, to be removed from the surface, the symmetry of the arrangement of the surface atoms will be destroyed This disturbance of the surface will certainly have an effect on the balance of forces holding the adjacent atoms. These atoms, therefore, will shift their positions. The neighboring carbon atoms (with their oxygen atoms) will then be held to the surface by a force which is *different* from that obtaining before the first CO_2 was removed.

Now if this force has been *strengthened*, then the adjacent molecules of CO_2 will be less likely to leave than others further from the disturbed region. Therefore, if the crystal is sufficiently heated, CO_2 would leave from all portions of the surface and a *solid solution* of CaO in $CaCO_3$ would be found. On the other hand if the removal of one CO_2 molecule sufficiently *weakens* the force by which the adjacent ones are held, then the CO_2 molecules will leave the surface only from positions adjacent to those from which they have already left. Under these conditions a separate phase of CaO would grow, starting from the point (nucleus) where the first CO_2 molecule left the surface.

We may therefore conclude, in the case of the dissociation of calcium carbonate that the removal of a CO_2 molecule causes a weakening of the forces by which adjacent molecules are held, whereas in the case of the dissociation of ferric oxide the removal of an oxygen atom does not weaken the forces holding the adjacent oxygen atoms.

When a molecule of CO_2 strikes a surface of the CaO phase it presumably condenses and may be held to the surface by forces no different in kind from those holding the calcite crystal together. However, if the removal of one CO_2 molecule from a surface weakens the forces by which adjacent ones are held, it is probable that the forces acting on a single CO_2 molecule in the midst of a surface of CaO would be extremely weak. Therefore, the CO_2 molecule would remain on such a surface such a short time, that the total number present in the CaO phase would not be of importance.

If, on the other hand, the forces holding the CO_2 molecule in the CaO phase were at all comparable with those acting at the boundary of the $CaCO_3$ phase, then we should have a variable phase, consisting of a solid solution of CO_2 in CaO, together with a constant phase of $CaCO_3$.

It is readily seen that the mechanism we have assumed, is capable of accounting for the different kinds of heterogeneous equilibria covered by the Phase Rule.

When there are two solid phases of constant composition and a gas, as in the dissociation of calcium carbonate, it follows directly from this mechanism

Digitized by Google Original from UNIVERSITY OF MICHIGAN

that the pressure of the gas is dependent only on the temperature and not on the relative proportions of the phases.

Thus the rate at which $CaCO_3$ dissociates is proportional to the number of *$CaCO_3$ groups adjacent to empty spaces*, while the rate at which $CaCO_3$ is formed is proportional to the pressure of CO_2 and to the number of *empty spaces adjacent to $CaCO_3$ groups*. Therefore, the pressure must be constant at a given temperature.[1]

This theory of the mechanism of heterogeneous equilibria appears to be particularly useful in accounting for various conditions not usually predicted by the Phase Rule.

Faraday[2] noted a case that fully justifies the assumption that in some equilibria the reaction can occur only when the surface has been disturbed. To quote from Faraday: "As a curious illustration of the influences of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulfate of soda having no part of their surfaces broken, be preserved from extrenal violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September, 1827 to January, 1833; and crystals of sulfate of soda from May, 1832 to the present time, November, 1833. If any part of the surface were scratched or broken, then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper."

It is well known that there is often great difficulty in removing the last traces of water of crystallization from a substance even when the hydrate gives a definite vapor pressure. According to the theory given above, the velocity of the dissociation is proportional to the area of the boundary between the phases. This boundary will usually have its maximum extent when both phases are present in more or less equivalent amounts. But the great difficulty in removing the last traces is undoubtedly due to the formation of solid solutions (adsorption!). Let us consider a crystalline substance AB which dissociates into a solid phase A and a gas B. The dissociation of AB and the recombination of A with B takes place most easily at the boundary between the phases AB and A. However, in general, we should expect that A and B also combine throughout the phase A, but that this compound is more unstable, and therefore dissociates at a higher rate. The rate at which A and B combine in this way in a unit volume

[1] Since developing the above theory of the mechanism of such heterogeneous equilibria I have found that this subject has been treated by A. Thiel (*Sitzber. d. Ges. zur. Beforderung d. gesamt. Naturwiss. in Marburg* (1913); *C. A.* **8**, 2284 (1914)). Thiel accepts as an axiom the relation given by Equation 12 and hence concludes that θ_1/θ_2 is necessarily constant at a given temperature. This result is at complete variance with the theory given above, and, in the writer's opinion, is wholly unsupported by experimental evidence. In a subsequent paper the writer expects to discuss Thiel's theory in more detail.

[2] "Experimental Researches", page 109, Everyman's Library Edition.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

of the phase A, will be proportional to the pressure p, while the rate at which it dissociates will be proportional to the concentration of B in A. By equating the two rates we see that the concentration of B in A should be proportional to the pressure of B.

There will, therefore, be the same kind of difficulty in removing the last trace of B from A as there is in producing a perfect vacuum.

The tendency of different substances to form these solid solutions will depend upon the extent to which the removal of one molecule of B from the phase AB affects the forces holding the adjacent molecules of B in AB.

It is a common experience that substances that are too thoroughly dehydrated are poor absorbers of moisture. A familiar example is overburnt lime or plaster of Paris. In some cases this phenomena may be due to a decrease in the porosity of the substance by sintering, but there is much evidence that this is not always the explanation.

According to the theory given above, the rate at which a partially dehydrated substance (which has a definite vapor pressure of moisture) will absorb moisture, should be proportional to the extent of the boundary between the hydrated and dehydrated phases. According to this simple theory a thoroughly dehydrated substance should be incapable of absorbing any moisture. However, in general, there is no reason why vapor should not be slowly absorbed to form a solid solution even with a dehydrated substance. Gradually nuclei would develop in this solid solution and the hydrated phase would appear. The rate of absorbtion of moisture would then rapidly increase as the surface area of the hydrated phase grows.

Adsorption of Gases by Solids

Unless the molecules of a gas which may strike a solid surface *all* rebound elastically there will necessarily be a higher concentration of molecules of the gas in the surface layer of the solid than in the body of the gas. If any molecules impinging on the surface are condensed, a certain time interval must elapse before they can evaporate. This time lag will bring about the accumulation of molecules in the surface layer, and may thus be looked upon as the cause of adsorption.

In the condensation of a vapor we have seen that the collisions are wholly inelastic, so that every molecule striking the surface condenses.

The reasons that have led us to this conclusion apply with nearly equal weight to gas molecules of almost any kind striking any surface[1].

[1] There is good experimental evidence that this rule is not of universal application. When hydrogen molecules strike surfaces at room temperature apparently something like 80% are diffusely reflected. This probably represents nearly the extreme case. However, even if 80% of the molecules are reflected, the adsorption of the gas on a surface is only 5 times less than it would be if none were reflected. Therefore every gas must be adsorbed to some extent on every surface. The evidence in regard to the reflection and condensation of gas molecules on surfaces is given in detail in a recent article (*Phys. Rev.* 8, 149 (1916)).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Let μ represent the number of gram molecules of gas striking each sq. cm of surface per second. The quantity μ can be readily calculated from the pressure by means of the following equation, derived from Equation (4)[1]

$$\mu = 43 \cdot 75 \times 10^{-6} \frac{p}{\sqrt{MT}} \tag{13}$$

The rate at which gas condenses on the surface will then be $a\mu$, where a is a quantity usually very close to unity (never exceeding unity).

If the surface is that of a crystal, there will be a definite number of spaces N_0, on each sq. cm of surface capable of holding adsorbed gas molecules. A greater number of gas molecules can only be adsorbed by the formation of additional layers of molecules. The forces acting between two layers of gas molecules will usually be very much less than those between the crystal surface and the first layer of molecules. The rate of evaporation in the second layer will, therefore, generally be so much more rapid than in the first, that the number of molecules in the second layer will be negligible[2]. When a gas molecule strikes a portion of the surface already covered, it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore, the rate of condensation of the gas on the crystal surface is $a\theta\mu$ where θ represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$ where ν_1 is the rate at which the gas would evaporate if the surface were completely covered and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal so we have

$$a\theta\mu = \nu_1\theta_1. \tag{14}$$

Furthermore

$$\theta + \theta_1 = 1. \tag{15}$$

Whence

$$\theta_1 = \frac{a\mu}{\nu_1 + a\mu}. \tag{16}$$

The quantity θ_1 is a measure of the amount of gas adsorbed. It should be noted that for low gas pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases θ_1 increases more slowly and finally the surface becomes saturated ($\theta_1 = 1$). These relations are in good qualitative agreement with known facts[3].

---

[1] The nomenclature used here is the same as that employed in a recent paper on the dissociation of hydrogen (*J. Am. Chem. Soc.* **38**, 1148 (1916)).

[2] The detailed development of this theory of adsorption, taking into account the evaporation from each of the layers and other complicating factors, will be published as Part II of the paper in the *Phys. Rev.* References to previous literature on the subject will be given at that time. The present paper deals principally with the chemical aspects of the theory.

[3] Equation 16 gives the amount of adsorption on a plane crystal surface. No reliable quantitative experimental data seem to be available for the adsorption of gases on such surfaces. The

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Equation 16 indicates that at low temperatures (small value of ν_1) the amount of adsorption should be large and nearly independent of the pressure, while at higher temperatures (large value of ν_1) the amount of adsorption should be small, and should be proportional to the pressure even at high pressures. These deductions also are in qualitative accord with experimental facts.

From Equation (16) we see that the tendency of a gas to be adsorbed on a surface is determined by ν_1, the rate of evaporation from the surface. This quantity in turn depends on the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance.

These forces will be of the same nature as those which hold solid bodies together. We may, therefore, profitably look upon them as chemical forces and apply our knowledge of the chemical properties in studying the phenomena of adsorption.

With a gas such as nitrogen, in which the atoms are mutually very thoroughly saturated, we know that there is only a weak field of force around the molecules. When a nitrogen molecule strikes a surface the forces holding it are only those due to weak secondary valence. It is to be expected, however, in general, that the forces by which molecules or atoms may be held on a surface, should show, for different substances, as great a range of intensity as is observed in the case of the forces acting inside of solid bodies.

Solid nitrogen is held together by comparatively weak forces, while the forces in solid carbon or tungsten are among the most powerful known. In the case of adsorbed films the magnitude of the forces should vary all the way from the weak forces observed with adsorbed nitrogen (or better helium) up to forces which are as intense as those holding together the atoms of the most stable chemical compounds. Just as we find either secondary or primary valences active between atoms in solids, so should we expect both kinds of valence to take part in the formation of adsorbed films. When we thus speak of adsorption as a chemical phenomena it should be remembered that we must also regard evaporation and condensation in general as chemical phenomena. The point to be emphasized is, that there is no real distinction between these so-called physical phenomena, and true chemical phenomena except that in general the "physical" phenomena depend on secondary valence rather than primary. Since, however, chemical phenomena involve secondary valence as well as primary, it seems best to classify all such phenomena as chemical. By so doing we do not in any way fail to recognize the close relationship between evaporation, condensation and the adsorption of the relatively inert gases.

This chemical theory of adsorption has received striking confirmation by many experiments in this laboratory.

---

writer is, therefore, undertaking measurements of this kind at present and will report the results at a later date. The theoretical reasons for believing that Equation 16 is not quantitatively applicable to adsorption by porous biodies such as charcoal will be discussed further on in this paper.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Experimental Evidence that Adsorption is a Chemical Phenomena

It has been found[1] that atomic hydrogen, produced by heating a metallic wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed on surfaces. According to the usual "physical" theory of adsorption by which the adsorbed film is assumed to be a layer of highly compressed gas we should expect that a gas of such low density as atomic hydrogen would be only slightly adsorbed. Furthermore, we should expect that an adsorption film in high vacuum would very rapidly reach equilibrium with its surroundings.

The experiments showed, however, that even in the highest vacuum quantities of hydrogen as large as 0.01 to 0.03 cubic mm (at atmospheric pressure) per sq. cm could be adsorbed on cold glass, and that this adsorbed film was remarkably stable, being able to remain unchanged on the surface for several days. To account for these adsorption phenomena it was suggested in 1912[2] that "perhaps the unsaturated chemical affinity of the atomic hydrogen gives it unusual tendencies to be adsorbed on surfaces." It was observed that the amount of atomic hydrogen which could accumulate on a given surface was strictly limited and it was shown that this was not due to a balance between the rate at which atomic hydrogen spontaneously escaped from the surface, and the rate at which it was deposited. On the contrary, it was shown that the amount was limited because, after a certain amount of atomic hydrogen was present on the surface, fresh atoms of hydrogen striking the surface combined with those already present, and thus removed them.

It is interesting to compare the amount of atomic hydrogen adsorbed on the glass with the amount necessary to form a layer one atom deep. If we take the diameter of the hydrogen atom to be the same as that of the molecule, namely about 2.5×10^{-8} cm, we may conclude that the number of hydrogen atoms per sq. cm needed to form a layer one atom deep is about 1.6×10^{15}. This corresponds to 0.032 cubic mm of molecular hydrogen at 20° and one megabar pressure. The maximum amounts of atomic hydrogen which were found adsorbed on glass surfaces were of this same order of magnitude (0.01 to 0.03 cubic mm per sq. cm).

In a subsequent paper[3] it was shown that atomic hydrogen could diffuse several feet through glass tubes at room temperature, but could not pass even through a short tube cooled in liquid air. This may be taken as evidence that practically all hydrogen atoms striking a cold glass surface condense. With the glass cooled by liquid air these atoms do not evaporate at a perceptible rate, but from glass at room temperature they evaporate sufficiently rapidly to permit the passage of the atomic hydrogen through a long tube.

---

[1] Langmuir, *J. Am. Chem. Soc.* **34**, 1310 (1912).

[2] *Loc. cit.*, p. 1313.

[3] Freeman, *J. Am. Chem. Soc.* **35**, 927 (1913).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

The experiments with atomic hydrogen thus furnish evidence that

1. The adsorption is determined by chemical affinity.
2. The adsorbed layer does not exceed one atom in thickness.
3. Hydrogen atoms striking glass surfaces are not reflected.

Similar evidence has been obtained from experiments with tungsten filaments in oxygen at low pressures. It was shown[1] that 15% of all oxygen molecules striking a tungsten filament at 2770°K react with it to form WO_3. More recent experiments (as yet unpublished) have shown that this coefficient continues to increase at higher temperatures, so that at 3300°K about 50% of all the oxygen molecules which strike the filament react with it to form WO_3. Since there are three atoms of oxygen in WO_3, and only two in the oxygen molecule, it is evident that *at least* one-half of the tungsten surface even at 3300°K must be covered with oxygen in some form. When we consider that the pressure of oxygen in these experiments was usually not over 5 bars we realize the extraordinary stability of the film, and are thus led to believe that the oxygen atoms are held by chemical forces to the tungsten atoms which form the lattice structure of the tungsten crystals.

It is very evident that the adsorbed film does not consist of tungsten oxide WO_3, since this substance distills very rapidly from the filament even at temperatures as low as 1200°K. The film has no perceptible effect on the optical properties of the tungsten surface, since low pressures of oxygen do not cause any perceptible change in the characteristics (volts, amperes, candle-power) of the tungsten filament.

The existance of this oxygen layer on a tungsten filament in oxygen at low pressure, shows itself in many other ways Thus a pressure of 0.001 bar of oxygen lowers the electron emission from a tungsten filament at 1800° to a very small fraction of its normal value. Even more striking evidence has been recently found in connection with experiments (as yet unpublished) with tungsten filaments in mixtures of various gases at low pressures. It is found that a tungsten filament at 1500°K in a mixture of oxygen and hydrogen reacts with the oxygen exactly as if no hydrogen were present. While this oxidation of the tungsten is going on, none of the hydrogen reacts with the oxygen, and the hydrogen does not reduce any of the tungsten oxide[2] formed, nor is any atomic hydrogen produced. However, after all of the oxygen has been used up (partial pressure reduced to less than 0.01 bar) the hydrogen *suddenly* begins to disappear by being dissociated into atoms which then react with the WO_3 previously deposited on the bulb.

Simultaneous measurements of the electron emission show that this emission increases suddenly at the same moment at which the hydrogen begins to disappear.

---

[1] Langmuir, *J. Am. Chem. Soc.* **35**, 105 (1913).

[2] This is especially remarkable since WO_3 is readily reduced by hydrogen at atmospheric pressure at temperatures as low as 500°.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

This experiment proves:

1. That in presence of even 0.01 bar of oxygen the surface of the tungsten at 1500°K is practically completely covered with oxygen.

2. That this layer of oxygen will not react with hydrogen even at 1500°K.

3. That such a layer of oxygen prevents the formation of atomic hydrogen.

4. That the decrease in electron emission produced by oxygen is due to the same cause as that which prevents the dissociation of hydrogen.

It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide, or a film of highly compressed gas. The facts are in good accord, however, with the theory that the oxygen atoms are chemically combined with the tungsten atoms. From this viewpoint the two primary valences of the oxygen are turned downwards, and are saturated by the tungsten, so that a hydrogen molecule striking the surface cannot react with the oxygen, and cannot come in contact with the tungsten. The hexavalent tungsten atoms, on the other hand, are not saturated by the oxygen, so that they are held firmly to the underlying layer of tungsten atoms. Only when the tungsten atoms on the surface become saturated by taking up two other oxygen atoms do they cease to be held to the other tungsten atoms, and thus evaporate off as WO_3.[1]

The stability of the oxygen layer is due to the strength of the chemical union between oxygen and tungsten atoms, which results in a very slow rate of evaporation of the oxygen atoms from the surface.

The action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a *catalytic poison*. It has been shown previously[2] that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500°K is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Now if this adsorbed oxygen were present on the surface as a layer of com-

---

[1] The fact that the tungsten atoms leave the surface only after they have been completely saturated chemically seems to be an example of a general tendency. Thus when tungsten is heated in chlorine at very low pressures the hexachloride WCl_6 only is formed, although several stable lower chlorides of tungsten exist. When Pt is heated at high temperatures in oxygen at moderate pressures the oxide PtO_2 distills from the surface, while an osmium filament in oxygen at low pressures gives OsO_4. Molybdenum in oxygen gives only MoO_3.

[2] *J. Am. Chem. Soc.* **38**, 1145 (1916).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

pressed gas[1] it would be inconceivable that it should not react at all with hydrogen at a temperature of 1500°K. Even if we should regard the adsorbed layer as consisting of adsorbed tungsten oxide we would be no nearer an explanation, for tungsten oxide is readily reduced to metallic tungsten by hydrogen at temperatures of 500°. We should have to say, with Bancroft, that the oxide is stabilized by adsorption. But, of course, this is a mere description and not an explanation of the phenomena.

It is very clear that the oxygen by being adsorbed has undergone a complete change in chemical properties and it is certainly not logical to consider that this has been brought about by a mere compression of the gas into a surface layer.

If, however, we assume that the oxygen atoms are chemically combined to the mass of the tungsten filament and form a *continuous* surface layer, all of the observed facts are readily accounted for. The oxygen atoms are saturated chemically by the tungsten (primary valence) and the field of force holding the oxygen atoms lies wholly below the surface where hydrogen molecules cannot reach it. When the pressure of oxygen falls so low that the supply of this gas at the surface is not sufficient to make up for the loss by evaporation, then gaps are formed in the continuous covering and the hydrogen is then able to make a *flank attack* on the oxygen. In this way the oxygen covering is *suddenly* removed when the pressure of oxygen falls below a certain critical value, and the dissociation of hydrogen, therefore, begins at once.[2]

The resemblance between the action of oxygen on a tungsten filament and the phenomena of electrochemical passivity is very striking, so much so, in fact, that the mechanism of passivity is probably similar to that of the effects described above[3].

According to this theory the effect of oxygen in poisoning the catalytic activity of tungsten is due to the formation of an exceptionally stable film of oxygen which is combined with and completely covers the surface of the tungsten.

The effects of the poisoning of tungsten by oxygen are also to be seen in many other reactions in gases at low pressures (10–100 bars), of which the following may be briefly mentioned.

---

[1] The commonly accepted theories of adsorption are based upon the assumption that there is a transition layer (van der Waals) in which the density varies gradually from that of the solid or liquid phase to that of the surrounding gas. Eucken (*Verh. deut. physik. Ges.* **16**, 345 (1914)), for example, considers that this transition layer is a sort of miniature atmosphere. Bakker (*Z. physik. Chem.* **89**, 1 (1915)) has a similar theory to account for surface-tension phenomena.

[2] The strongest evidence of the correctness of this theory is obtained from experiments at higher filament temperatures than 1700°K. The hydrogen and oxygen then begin to react with each other on the surface of the filament. The further development of this theory is reserved for a future paper, in which the detailed experimental results will be published.

[3] An outline of this theory of passivity together with a brief description of the experiments with mixtures of oxygen and hydrogen in contact with a hot tungsten filament was given by the writer in a discussion of Bennett and Burnham's paper on Passivity, at the Washington meeting of the American Electrochemical Society, April 28, 1916. This discussion has been published in Vol. 29 of the Transactions.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

When a tungsten filament is heated in a mixture of carbon monoxide and oxygen, tungsten is oxidized just as if no carbon monoxide were present. None of the CO reacts with the oxygen even when the filament is heated as high as 2800°K whereas hydrogen begins to react with oxygen in contact with a tungsten filament when the temperature exceeds about 1700°K. Evidently CO will not combine with oxygen adsorbed on a heated tungsten filament even if it has a chance to make a "flank attack".

Mixtures of methane and oxygen at low pressures do not react with one another in contact with tungsten at 1500° or even 1800°K but the tungsten is oxidized to form WO_3 as in the previous cases. In absence of oxygen, methane is gradually decomposed, setting free hydrogen, while the carbon is taken up by the tungsten filament, forming a solid solution. Even this action is prevented by the presence of traces of oxygen. On the other hand, if the filament is first heated in methane, so that it has taken up carbon, and then oxygen is admitted, the oxygen reacts with the carbon in the filament forming CO, and until all the carbon from the surface layers has been removed, the oxygen does not react with the tungsten. This proves that when carbon is taken up by tungsten some of the carbon remains as an adsorbed layer of carbon atoms.

Dry ammonia at low pressures is decomposed fairly rapidly by a tungsten filament at 1000°K but with a platinum filament the same rate of decomposition only occurs at a temperature of nearly 1400°K. In the presence of small amounts of oxygen, however, the tungsten filament fails to decompose ammonia even at 1200°K. At 1300°K the tungsten oxidizes just as if the ammonia were absent, the oxide WO_3 distilling to the bulb. Some of the ammonia seems to react with the oxygen, but with an excess of ammonia this reaction goes on slowly until the oxygen is consumed, and the remainder of the ammonia is then rapidly dissociated. The oxygen thus poisons the tungsten even in the case of the simple dissociation of ammonia by heat. In contact with platinum, however, ammonia and oxygen react together at a temperature well below 1000°K. Particularly interesting effects are observed when a tungsten or platinum filament is heated in mixtures of cyanogen and oxygen. In this case, with a filament at 1500°K the oxidation of the tungsten is largely prevented until the cyanogen has been slowly oxidized to carbon monoxide and nitrogen. If there is an excess of oxygen this then reacts with the tungsten when the supply of cyanogen is used up. Any excess of cyanogen is decomposed by the filament giving nitrogen, the carbon being taken up by the filament. Thus cyanogen may be looked upon as having a stronger poisoning effect on tungsten than oxygen has.

It is well known that cyanogen poisons the catalytic activity of platinum. Experiments at low pressures furnish a remarkable demonstration of this fact.

A platinum filament at a temperature of 600°K causes carbon monoxide and oxygen to combine rapidly, the carbon monoxide, however, itself, acting as a catalytic poison[1]. At higher temperatures (900°K) the poisoning effect

[1] Langmuir, *J. Am. Chem. Soc.* **37**, 1163 (1915).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

of the carbon monoxide disappears and the velocity of the reaction becomes enormously high, being then limited only by the rate at which the two gases can come into contact with the platinum surface, according to Equation (4).

But if a trace of cyanogen is added to the mixture of oxygen and carbon monoxide (at a pressure of 10 bars) the catalytic action of the platinum disappears completely even at 900°K. By raising the temperature to about 1000° the cyanogen reacts with the oxygen to form nitrogen and carbon monoxide. As soon as the cyanogen is all oxidized the catalytic activity of the platinum is restored and the oxygen and carbon monoxide then react rapidly to form carbon dioxide.

The catalytic effect of platinum on the reaction between oxygen and hydrogen is also poisoned by traces of cyanogen. If the temperature of the platinum is then raised, the cyanogen and hydrogen react together to form hydrocyanic acid.

The fact that these low pressures of cyanogen (or oxygen) can exert such a powerful poisoning effect is proof that adsorbed films of great stability are formed, in other words, films in which the rate of evaporation of the adsorbed molecules is remarkably low. The effect of these poisons is thus merely to cover up the active surface.

The property of cyanogen in poisoning metallic catalyzers is thus closely related to the chemical facts that cyanogen forms very stable compounds with metals, and shows an unusual tendency to form complex salts. The cyanogen radical is one in which both the primary and the secondary valences are strongly developed.

Water vapor has the same effect in poisoning the catalytic activity of tungsten that oxygen has. A partial pressure of 0.4 bar of water vapor (vapor pressure of water at −78°) is sufficient to prevent the dissociation of hydrogen by a tungsten filament at 1500°K.

It is a remarkable fact that carbon dioxide, although it oxidizes a tungsten filament to form WO_3, does not have any effect upon the rate of dissociation of hydrogen. We must, therefore, conclude in this case that only a very small fraction of the tungsten surface is covered by adsorbed oxygen. This conclusion is also supported by the fact that the rate of oxidation of tungsten by carbon dioxide is extremely slow compared to the rate of oxidation by oxygen. We shall see that further evidence of the same kind is furnished by measurements of the electron emission. However, since the oxygen from at least two molecules of carbon dioxide is needed to produce a molecule of WO_3, it is certain that the reaction depends upon the presence of adsorbed oxygen partially covering the surface. The velocity of the reaction between carbon dioxide and tungsten seems to be approximately proportional to the square root of the pressure of CO_2 and inversely proportional to the pressure of carbon monoxide.

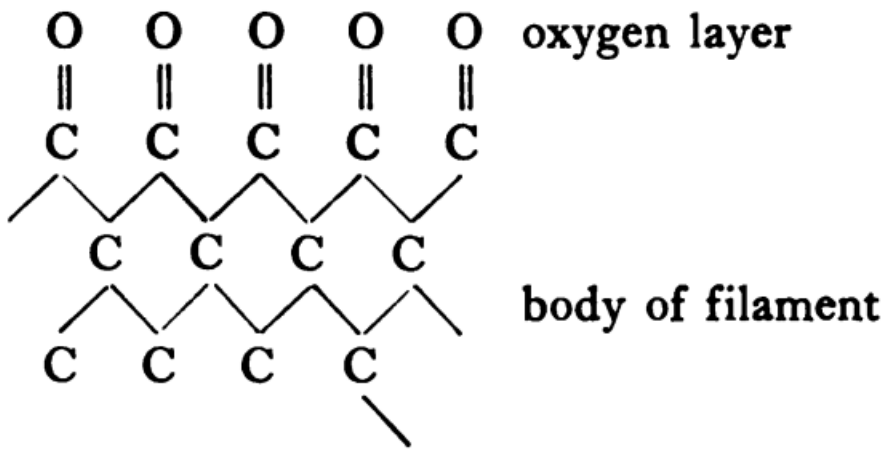
When molybdenum filaments are heated in oxygen at low pressures the filaments become tarnished unless the temperature is maintained above 1500°K.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Above this temperature the surface of the filament remains apparently clean, and the oxide formed, MoO_3, distills to the bulb. With tungsten, notwithstanding the fact that WO_3 is much less voltaile than MoO_3, it is only necessary to keep the temperature above about 1250° in order to have a clean surface.

Although oxygen is clearly adsorbed on molybdenum, it appears that the stability of the film is much less than that of the corresponding film on tungsten. This is shown not only by the electron emission (see below), but by the comparatively small effect of oxygen in poisoning the catalytic activity of molybdenum. Thus when molybdenum is heated to a temperature between 1500 and 1800°K in a mixture of oxygen and hydrogen, it is found that the hydrogen disappears slowly until the oxygen is all used up, by reacting with the molybdenum. After that the rate of disappearance of the hydrogen is much greater. The fact that a part of the hydrogen disappears before the oxygen is consumed indicates that the poisoning effect of the oxygen is not complete.

Experiments with carbon filaments in oxygen, and in carbon monoxide or dioxide[1] have shown that oxygen acts as a catalytic poison, on the reaction between oxygen and carbon, and on that between carbon dioxide and carbon. It was also proved that this poisoning effect is due to a remarkably stable film of adsorbed oxygen, so stable in fact that the filament must be heated in a good vacuum for nearly half an hour at 2300°K in order to distill it off. In this case there is very clear evidence that this film consists of oxygen atoms chemically combined by primary valences to the carbon atoms forming the body of the filament, according to the formula



A very peculiar case of adsorption occurs when a tungsten filament is heated to about 2700°K in a low pressure of carbon monoxide contained in a bulb cooled by liquid air[2].

With the bulb at this temperature the tungsten filament is attacked by the CO and a very stable adsorbed film is formed on the filament. This distills off at a constant rate (independent of the pressure of CO) taking the tungsten with it as a compound of the composition WCO. The most remarkable fact is that when the temperature of the bulb is raised to 20° or above, the CO no

---

[1] *J. Am. Chem. Soc.* **37**, 1154 (1915).

[2] A brief preliminary account of these experiments was published in *J. Am. Chem. Soc.* **37**, 1160 (1915). A more detailed paper will be presented later.

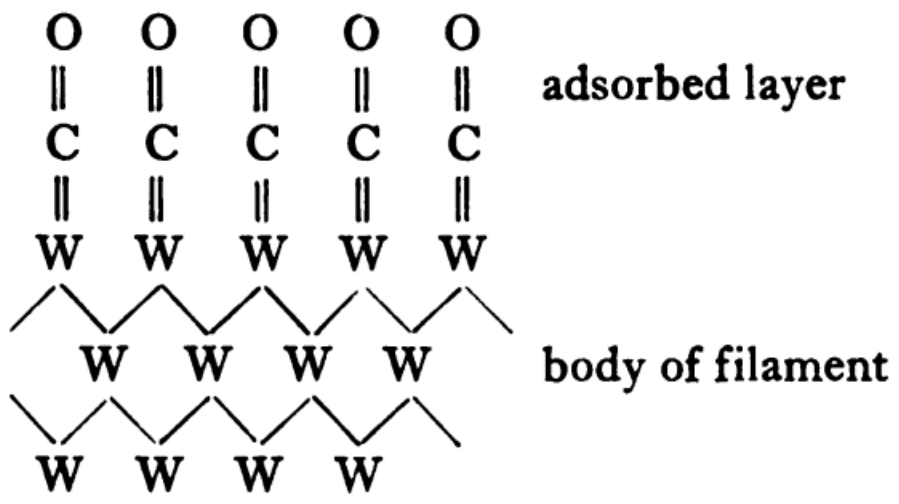
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

longer attacks the tungsten of the filament, but combines only with the tungsten which evaporates from the filament, still forming the compound WCO.

Before attempting to look for the probable mechanism of this action let us consider one more case of adsorption: that of nitrogen by *molybdenum vapor*. When a molybdenum filament is heated to 2200°K in nitrogen contained in a bulb cooled in liquid air, nearly every molybdenum atom evaporating from the filament combines with the *first* nitrogen molecule which it strikes to form a compound MoN_2 (stable at 360° in a vacuum). When the bulb is at room temperature the molybdenum atoms still combine with the first nitrogen molecule they strike, but most of the molecules thus formed are so unstable that they decompose when they strike the bulb, giving nitrogen and a spongy molybdenum deposit.

Thus when the nitrogen is at low temperature the compound appears to be MoN_2 in which the atoms are held by primary valence, while the compound formed with the nitrogen at higher temperatures is $Mo:N_2$, in which the nitrogen and molybdenum are held by secondary valence. This seems then to be a kind of adsorption of one gas by another.

A somewhat similar explanation seems necessary for the reaction between tungsten and carbon monoxide. Thus when carbon monoxide molecules of low velocity and low internal energy (low temperature) strike the surface of the filament they combine with it by primary valences to form a stable structure, probably as follows:



The strength of the union between the oxygen and carbon, and between the tungsten and carbon, is so great, that the whole group WCO distills off as a single molecule. The fact that the tungsten is partially saturated by the carbon should make this group somewhat more volatile than the tungsten itself. As a matter of fact the rate of evaporation of the WCO from the surface is only about five times greater than that of tungsten.

When the temperature of the bulb is higher, so that the CO molecules possess more internal energy (and a higher velocity) the CO is incapable of combining with the solid tungsten in the above manner. We must still assume that nearly every CO molecule which strikes the filament condenses on it, but that the union in this case is by secondary valence, so that the molecule almost immediately distills off again.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

A more thorough study of this reaction may throw some light on the paradox that the residual valence of CO is small, although this substance contains a divalent carbon atom.

The Effect of Gases on the Electron Emission from Heated Metals as Evidence of the Presence of Stable Adsorbed Films

The effect of adsorbed films of the thickness of a single molecule on the electron emission from heated tungsten filaments was described by the writer in 1913[1]. A little later[2] the following theory of the effect was proposed. "The decrease in the electron emission from a hot cathode caused by certain gases is due to the formation of a film on the surface of the cathode. Whether this film consists of adsorbed gas, or of a chemical compound of the gas with the cathode material, is not definitely established, but most of the evidence is in favor of the latter view. The amount by which the electron emission is affected depends on the *extent* to which the surface is covered. The film should be looked upon as consisting of a single layer of molecules, or at most, of a very few layers. The extent to which the surface of the cathode is covered by the film depends upon: (1) The rate of formation of the film. (2). The rate of destruction of the film," etc.

The more recent work on chemical reactions at low pressures, and further experiments on electron emission, have furnished abundant evidence of the correctness of the above viewpoint, and have fully verified the conclusion that the film is held to the surface by chemical forces.

In every case with tungsten, chemically inert gases have been found to be without effect on the electron emission, whereas nearly all gases that react with the tungsten lower the emission.

The decrease of the electron current produced by a gas is thus caused by the formation of an adsorbed film of great stability, which covers the surface. The evidence is very strong that the electron emission at a given temperature depends only on the nature of the layer of atoms forming the actual surface of the filament. Here again we have proof of the absence of a transition layer in which the density varies gradually from that of the filament to that of the surrounding space.

The lowering of the electron emission of heated filaments by adsorbed films thus bears a close relationship to the effect of these films in poisoning the catalytic activity of the filament. Both effects are caused by a film of great stability which covers the surface. The following experimental evidence shows in fact, that there is a remarkable parallelism between the electron emission and the catalytic activity of a filament.

As has already been pointed out, oxygen enormously lowers the electron emission from tungsten. This effect of oxygen is in accord with its action as

---

[1] Langmuir, *Phys. Rev.* **2**, 450 (1913).

[2] *Physik Z.* **15**, 520 (1914).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

a catalytic poison for tungsten. Thus in mixtures of oxygen and hydrogen the electron emission undergoes a sudden increase at the moment at which the hydrogen begins to dissociate (after the consumption of all the oxygen).

It might be thought that the electron emission itself would have an effect on the chemical reactions occurring on the surface of a heated filament. But experiment has never shown any such direct effect. Thus the rate at which oxygen, hydrogen, carbon dioxide, and other gases disappear in contact with heated tungsten are found to be entirely independent of the thermionic currents. The presence of a negatively charged electrode close to the heated filament causes all electrons emitted to be driven back into the filament, but this does not affect the rate of disappearance of the gases. In some cases, however, electric discharges do cause the clean-up of gases, but this effect is due to the bombardment of the filament by positive ions, and not to the electron emission.

Nitrogen does not normally attack a tungsten filament at any temperature, although it combines (to form WN_2) with tungsten vapor as fast as this evaporates from the filament[1]. Similarly nitrogen has no effect on the electron emission from tungsten if low voltages are used in making the measurements of the thermionic current But if voltages high enough to cause ionization of the nitrogen are employed, then the tungsten is attacked by the rapidly moving positive nitrogen ions, and simultaneously the electron emission is greatly decreased, indicating that a film of adsorbed nitrogen is formed. If the filament is now allowed to cool to room temperature and the remaining nitrogen is pumped out, and the filament is then heated again to the same temperature as before, it is found that the electron emission is at first the same as it was in the presence of the nitrogen, showing that the electron emission is determined not by the gas around the filament, but by the film adsorbed on it. Gradually the adsorbed film distills off, and the electron emission returns to its normal value.

By the study of such lag effects, the rate of evaporation and the rate of formation of the adsorbed films can be measured with accuracy, and it has thus been proved that the fraction of the surface covered often depends upon a dynamic equilibrium.

The fact that the rate of evaporation of these films even at temperatures of 1800°K is slow enough to measure proves that they are remarkably stable.

Extremely interesting phenomena are observed after a tungsten filament has been heated in CH_4 or C_2N_2, or other gas which gives up carbon to the filament. The most minute trace of carbon[2], in the surface of the filament cuts down the electron emission to about one-third of that of an uncontaminated filament. But a filament which has taken up carbon is no longer sensitive to the effect of bombardment by positive nitrogen ions. In other words nitrogen has no effect on the electron emission from such a filament even if high anode

---

[1] *J. Am. Chem. Soc.* **35**, 931 (1913).

[2] Probably just enough to form a layer one atom deep over the surface of the filament is sufficient.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

voltages are used. Still more remarkable is the fact that oxygen instead of lowering the electron emission of a carbon-containing filament gradually raises it. The carbon is then gradually oxidized and the electron emission returns to the value corresponding to pure tungsten. Then when the carbon has all been removed, the oxygen begins to attack the tungsten and the electron emission suddenly decreases to one per cent or less of its former value. After the excess oxygen has been consumed it is found that the electron emission is again sensitive to the effect of bombardment by positive nitrogen ions, the thermionic current decreasing as the voltage is raised.

This experiment is an excellent demonstration of the closeness of the relationship between the electron emission and the chemical activity of the filament.

Another illustration is afforded by the fact that water-vapor, which reacts rapidly with tungsten, and poisons the tungsten surface, has as great an effect on the electron emission as oxygen, while carbon dioxide, which reacts slowly with tungsten, and is not a catalytic poison, has practically no effect on the electron emission.

So far we have considered the effects of gases on the electron emission from tungsten. Striking effects of another kind are obtained when the filament contains minute amounts of thorium[1]. If such a filament is heated in a very high vacuum to 2900°K for a short time and the electron emission at 1800°K is then measured, it is found that the emission is the same as that of pure tungsten. By now heating the filament a few minutes at a temperature between 2000° and 2500°K (preferably 2300°K), the electron emission at 1800°K is found to have increased enormously (more than 10,000 fold). By heating again to 2900° the emission returns to its normal value.

This effect is due to the formation of an adsorbed layer of thorium atoms on the surface of the filament. At 2900°K the thorium, being more volatile than tungsten, distills off the surface and leaves pure tungsten. At 2300°K however, the rate of distillation is not very marked, but the rate of diffusion of the thorium through the tungsten is sufficient to allow the accumulation of thorium atoms on the surface. At 1800° the rate of diffusion is negligible, so that if the thorium is distilled off a fresh supply does not diffuse to the surface.

The tendency of thorium to form an adsorbed film on tungsten is in accord with other properties of thorium. Gibb has shown that any substance which lowers the surface energy tends to be adsorbed on the surface. The Eötvös-Ramsay-Shields relation indicates that the surface energy of a substance at temperatures low compared to its critical temperature, should be approximately proportional to $T_c A^{-\frac{1}{3}}$ where T_c is the critical temperature and A is the atomic volume. Now the critical temperature of thorium must be lower than that of tungsten, since the vapor-pressure of thorium is considerably greater than

[1] An account of these phenomena was given before the American Phys. Soc., Oct. 31, 1914 (*Phys. Rev.* **4**, 544 (1914)). A paragraph describing the effect was given in a paper before the American Electrochemical Soc. (see *Trans. Am. Electrochem. Soc.* **29**, 353 (1916)).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

that of tungsten. The atomic volume of thorium is about 21, while that of tungsten is 9.6. Thus both T_c and A differ, for these metals, in such a way as to make the surface energy of thorium less than that of tungsten. Therefore, according to Gibb's rule thorium should tend to be adsorbed on the surface of tungsten.

By a study of the rate of growth of the adsorbed film at 2100°K and the rate of evaporation at 2700°K it has been possible to prove that the film grows until it is one atom deep but does not grow beyond this[1]. The real evidence in favor of these conclusions, however, can only be given in connection with a full discussion of the detailed experimental results. It is intended to publish these before long.

When oxygen is brought into contact with a tungsten filament (at 1900°K) coated with a layer of thorium atoms, the electron emission is suddenly decreased to a value far below that corresponding to pure tungsten. With tungsten the effect of oxygen in decreasing the emission disappears as soon as all the oxygen has been consumed. But with a thorium-coated filament the effect of oxygen is more permanent, so that the emission remains low even after all oxygen has been removed. Only by heating the filament to 2900° and following this by a treatment at 2300° can the activity be restored. This behavior is in accord with the known facts that thorium has an unusually strong affinity for oxygen.

In the case of this oxidized thorium-coated filament the adsorbed film evidently consists of a layer of thorium atoms covered by a layer of oxygen atoms. It should not be looked upon as a layer of adsorbed thorium oxide.

Interesting effects are observed if a small amount of methane is brought into contact with an oxidized thorium-coated tungsten filament at about 1900°K. The electron emission suddenly increases to that of pure thorium, and then as suddenly decreases to a value below that of pure tungsten. The methane reacts with the oxygen on the surface of the filament, forming carbon monoxide, which evaporates off, leaving the layer of thorium atoms. The excess of methane is then decomposed, and a layer of carbon atoms is formed on the surface of the filament, and covers the thorium atoms. The electron emission then becomes that of a carbon surface which is a little less than that of tungsten, notwithstanding the presence of thorium atoms just under the surface layer.

Kruger and Taege[2] have recently studied the effect of catalytic poisons on the photoelectric activity of platinum, using ultraviolet light. They find that minute traces of H_2S, HCN or CO very greatly decrease the photoelectric electron emission. The mechanism of this action is undoubtedly identical with

---

[1] That the layer is never more than one atom deep is readily proved by the fact that the activity of the film always begins to decrease *at once* at 2700° no matter how long it may have been previously heated at 2300°K.

[2] *Z. Electrochem.* **21**, 562 (1915).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

that of the effect on the thermionic electron emission. Debye[1] and Richardson[2] have shown that there is a very close relationship between the photoelectric and thermionic electron emission[3].

Adsorption Phenomena at Higher Gas Pressures

The effect of poisons on the activity of catalyzers is essentially the same with gases at atmospheric pressure as at lower pressures. There is every reason for believing that the theory of adsorption outlined in the preceding pages is applicable to the adsorption of gas at atmospheric pressures. In the second part of this paper we shall see that a similar theory also applies to adsorption in surface layers of liquids.

As the pressure of a gas increases the amount adsorbed on a plane surface should gradually increase until the surface becomes completely covered by a layer one molecule (or atom) deep. The surface thus becomes *saturated*. This is in full accord with experimental facts.

In the case of the adsorption of vapors at such high pressures that they approach the state of saturated vapors, there will be a tendency for the adsorbed film to become several molecules deep.

According to this theory it is very improbable that films more than one or two molecules deep would ever be held on a surface by adsorption, except with nearly saturated vapors. We must assume that after a layer two or three molecules deep is formed, the rate of evaporation of additional molecules would be nearly identical with that from the liquefied or solidified gas. If the vapor pressure were well below saturation, the rate at which such additional molecules would condense in the surface would be much less than rate at which they would evaporate. The adsorbed film would thus grow thinner.

There is considerable experimental evidence that the amount of moisture taken up by glass surfaces is greatly in excess of the amount needed to form a layer one molecule deep.

When a 40-watt incandescent lamp bulb is heated to 500° for several hours (after having been exhausted and dried out at room temperature) it gives off about 0.45 cc. of water vapor, 0.030 cc. of carbon dioxide, and 0.005 cc. of nitrogen[4]. The internal surface of this bulb was about 200 sq. cm. The number of molecules of gas given off per sq. cm was thus 56×10^{15} molecules of H_2O; 37×10^{15} molecules of CO_2 and 0.6×10^{15} molecules of N_2. If we calculate the number of molecules of each of the gases necessary to cover a sq. cm one molecule deep (taking the molecules to be cubical in shape) we find 1.0×10^{15} for H_2O; 0.77×10^{15} for CO_2 and 0.67×10^{15} for N_2. Thus the quantities of gas

---

[1] *Ann. Phys.* **33**, 441 (1910).

[2] *Phil. Mag.* **23**, 266, 615 (1912); **24**, 570 (1912).

[3] For a review of the recent work on this subject and its relation to contact potentials see a paper by Langmuir, *Trans. Am. Electrochem. Soc.* **29**, 341 (1916).

[4] Langmuir, *Trans. Am. Inst. Elec. Eng.* **32**, 1921 (1913).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

obtained from this bulb correspond to: a layer of water 55 molecules deep, a layer of carbon dioxide 4.8 molecules deep and a layer of nitrogen 0.9 molecule deep.

The adsorption(?) of water vapor by pulverized synthetic quartz and anorthite has been studied by J. R. Katz[1]. The amount of water taken up reaches a fairly definite limit when the vapor pressure of the water is about 0.7 of the saturated vapor. The quantities of water adsorbed per sq. cm of surface under these conditions were 1.3×10^{-6} grams for quartz and 6.2×10^{-6} grams for anorthite. These correspond to layers of water 43 and 205 molecules deep, respectively. Freundlich[2] reviews the literature on the thickness of adsorbed films, and comes to the conclusion that these films in general range from 10^{-7} to 10^{-6} cm in thickness. Since the diameters of atoms and molecules usually lie between 2×10^{-8} and 5×10^{-8} cm, the adsorbed films, according to Freundlich, should be many molecules thick. The evidence on which this conclusion is based is very meagre, and for the most part is quite indirect. The best data referred to are probably those of Ihmori[3]. According to Freundlich, Ihmori "found with polished metals (brass, steel, etc.) thicknesses for the surface layer of water ranging between 3 and 10×10^{-7} cm; and with quartz, an average thickness of 22×10^{-7} cm."

However, by referring to Ihmori's original article, it appears that this investigator found that the amount of "adsorbed" moisture increased greatly (about 10 fold) if the metal had previously been allowed to stand in the air for a few weeks. With carefully cleaned (polished or ignited) platinum he could not detect any adsorption whatever, that is, the adsorbed film in this case must have been less than 2×10^{-8} cm thick. Ihmori says "the small amount of water adsorbed by the metals designated as 'polished' is, perhaps, due to the presence of a thin film of oxide."

In Ihmori's experiments the pressure of the water vapor was about 92% of that at saturation.

From the cases considered above it appears that certain surfaces adsorb moisture in quantities very large compared to that necessary to form a layer one molecule thick. There is no evidence, however, that in any of the cases studied the phenomena is a true adsorption.

The term adsorption should be restricted to gas taken up *on a surface* without any penetration of the gas molecules between the atoms or molecules of the solid surface. The theory of adsorption developed in this paper indicates that the amount thus truly adsorbed should never exceed a layer one or two molecules in thickness.

But there is no reason whatever why molecules of gas or vapor should not penetrate in between atoms of the surface and thus be absorbed. Dried jellies

---

[1] *Proc. Amsterdam Acad.* **15**, 445 (1912).

[2] *Kapillarchemie*, Leipzig (1909), p. 265.

[3] *Wied. Ann.* **31**, 1006 (1887).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

can absorb large quantities of moisture, and dehydrated salts usually absorb moisture even when no definite hydrates are formed (solid solutions).

The absorption of moisture by a surface of glass is to be looked upon as a process of solution of the water into the glass. Dried sodium silicate absorbs moisture in this way in very large quantities, and it is not at all surprising that this property should not be wholly lost, when lime and other oxides are fused with the alkali silicate. The whole behavior of glass surfaces in giving up their moisture confirms this theory that the moisture penetrates to a very considerable depth into the surface. The remarkable slowness with which the moisture is given up on heating, and the length of time needed for the reabsorption of the moisture indicate that we are not dealing with a true adsorption phenomena.

In the case of Katz's experiments with anorthite and quartz, there is probably also a penetration of the moisture into the crystal substance. It is, however, quite possible that what he measured was the moisture actually condensed as liquid in the fine capillary spaces between the grains of the extremely fine powder experimented with.

We may safely assume that water vapor would not penetrate at all into a metal, so that a *clean* metal surface should never take up more moisture than enough to form a layer one molecule deep. This is in accord with Ihmori's results, since he could not detect absorption of moisture by platinum. The other metals used by Ihmori all oxidize in contact with air. The oxide layer formed is usually thick enough to see. When we consider that a film of metallic *tungsten* ten atoms thick only absorbs about 20% of the light striking it, it is evident that a film of *oxide* thick enough to see must be of very great thickness compared to that of a molecule. Furthermore, such a film must be quite porous, since the oxygen required for its growth must have diffused through it. It is, therefore, not remarkable that relatively large quantities of moisture are absorbed by such films.

Adsorption by Porous Bodies

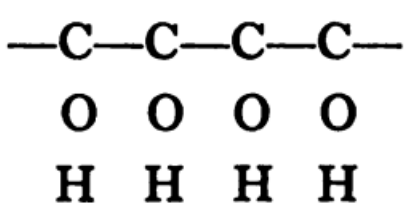
Nearly all quantatitive measurements of the adsorption of gases by solids have been made with porous bodies such as charcoal. In these cases it is impossible to know definitely the area on which adsorption takes place.

It is often assumed that the surface of even a polished metal is porous to such an extent that its "true surface" is much greater than its apparent surface. As far as the writer knows, there is no experimental evidence to support any such assumption and theoretical considerations would make it seem extremely improbable. The strong surface forces (quite analogous to that in liquids) would tend to make the atoms in the surfaces of solids arrange themselves in such a way as to make the total surface a minimum. Therefore, in the absence of definite causes which produce a porous structure (such as those considered below), we should assume that the atoms of the surfaces are packed closely together and are arranged with considerable regularity. Thus a surface of glass should not be considered as porous, although it is capable of absorbing

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

considerable quantities of moisture. The absorption is here a solution process, in other words, a chemical change by which the water molecules become combined (secondary valence) with the atoms of groups of atoms forming the glass. There is no more reason for assuming a porous structure than there is in the case of a liquid.

Truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibers of cellulose from which charcoal is usually formed probably consist of practically endless groups of atoms



held together by primary valences in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat, the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. The porosity of the charcoal thus undoubtedly extends down to atomic dimensions. The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon.

It is evident that with a structure of this kind, it is meaningless to talk about the surface on which adsorption can take place. With plane surfaces, we have seen that adsorption is usually limited to the formation of a layer one molecule deep, so that we can estimate the maximum adsorption from the extent of the surface. With charcoal, on the other hand, there is no definite surface which can be covered by a layer one molecule deep. Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom. Under these conditions there will be some spaces from which evaporation of adsorbed molecules would occur very slowly and others from which it would take place much more rapidly. There would be, however, a fairly sharp limit to the number of molecules which could come into intimate contact with carbon atoms. This limit would correspond to the saturated state observable in adsorption even by porous bodies. But it is evident that Equations (14), (15) and (16) which apply to adsorption by plane surfaces, could not apply to adsorption by charcoal. The real reason for this failure is that we can no longer assume (as in the derivation of Equation 14) that the rate at which the adsorbed gas evaporates from the surface is proportional to the amount present on the surface.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Strong support for the above views on the structure of porous bodies and the nature of adsorption by them is furnished by experiments in which molybdenum filaments were vaporized in nitrogen at low pressures. These experiments will be described in a future publication.[1]

General Conclusions Regarding Kinetics of Heterogeneous Reactions

The theory developed in this paper and the experimental work on electron emission and chemical reactions at low pressures leads to the following conclusion: ***In a heterogeneous chemical reaction, the activity of a surface depends in general upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer.*** The atoms forming the second layer below the surface are of importance only insofar as they determine the arrangement of the surface atoms.

In the second part of this paper, it will be shown that the surface tension in liquids depends upon these same factors, in other words, it depends primarily upon the *surface layer of atoms* and only secondarily upon the group molecules of which these atoms form parts.

According to this view, the velocity of reactions in general is not limited by the rate of diffusion through an adsorbed film, but by the rate at which the molecules strike (according to Equation 4) against that portion of the surface which is active. Of course, there are many chemical processes which are actually limited by physical factors, such as the rate of diffusion through layers of gas or moderately thick films covering the solids substances. The rusting of iron, the oxidation of aluminum, the solubility of very soluble salts, etc., are examples of this type. But there is no present justification for believing that such physical factors determine the velocity of the typical catalytic reactions.

This theory of heterogeneous reactions can be readily developed along quantitative lines. Some of the principles upon which this development is based have been outlined in a recent paper on the dissociation of hydrogen.[2] A brief, but more general treatment will, however, not be out of place here.

The velocity of a reaction usually depends on the fraction of the surface which is covered by adsorbed atoms or molecules. This in turn depends on the rate of condensation and on the rate of evaporation of the adsorbed substance. In the sections of this paper dealing with condensation and evaporation, we considered only the case where the vapor condensing and the surface on which condensation occurred, consisted of the same substance. In the case where different substances are involved, some additional factors must be taken into account.

---

[1] A brief preliminary description of these results was given in *J. Am. Chem. Soc.* **37**, 1159 (1915).

[2] *J. Am. Chem. Soc.* **38**, 1145 (1916).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Condensation.—The surface on which condensation occurs contains a definite number N_0 of elementary spaces, per unit area. Let θ be the fraction of these spaces which are unoccupied and θ_1 be the fraction occupied by adsorbed atoms or molecules.

If each molecule condensing requires only one elementary space, the rate of condensation will be equal to $\alpha\theta\mu$.[1] But it may happen that each molecule requires two such spaces before condensation can occur. The chance that one space will be vacant is θ, but the chance that two given spaces will be simultaneously vacant is θ^2. Therefore, the rate of condensation is equal to $\alpha\theta^2\mu$. In general, the rate of condensation will be $\alpha\theta^0\mu$ where n is an integer.

Evaporation.—In evaporation it may occur that two atoms must lie in adjacent positions in order that they may leave the surface together as a molecule. In such cases the rate of evaporation will be $\nu_1\theta_1^2$ instead of $\nu_1\theta_1$.

Chemical reactions may take place either between adjacent atoms on the surface or may occur when gas molecules strike molecules or atoms on the surface. In the former case the velocity of the reaction, in general, will be proportional to $\theta^n\theta_1^m\theta_2^p$ where θ_1 and θ_2 are the fractions of the surface covered by the reacting substances and n, m and p are integers. The reason for the occurrence of the factor θ^n in this expression is that the number of elementary spaces occupied by the products of the reaction may be greater than that occupied by the reacting substances. The reaction will thus only occur when vacant spaces are available.

We see that the reaction on surfaces will be governed by a "law of surface action" analogous to the "law of mass action." The velocity in both cases is proportional to a continued product of factors having integral exponents. A radical difference between the two laws exists in the presence of the factor θ^n in the case of reactions on surfaces.[2]

Let us consider a few simple special cases of heterogeneous reactions. To simplify the problem, we will assume that the velocity of the reaction is slow compared to the rate at which the gas condenses and evaporates from the surface. In other words, we will limit ourselves to a consideration of those cases where the velocity of the reaction is not fast enough to materially affect the equilibrium between the adsorbed film and the surrounding gas.

There are two types of cases to consider. First, those in which the adsorbed film covers only a very small fraction of the surface ($\theta = 1$). Secondly, those in which the surface is nearly completely covered by the adsorbed film.

---

[1] Compare with the derivation of Equation 14.

[2] Since $\theta+\theta_1+\theta_2+ \ldots = 1$ this law bears a close relationship to Reichinstein's "Constant Sum Hypothesis", which has been used to explain various kinds of passivity phenomena.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

First Case. Surface only Covered to a Small Extent

Let us consider a single gas which undergoes a chemical change (for example a dissociation) in contact with a solid body. The rate of condensation on the surface will be $\alpha_1\mu_1$ and the rate of evaporation of the unchanged gas will be $\nu_1\theta_1^n$ where n represents the number of elementary spaces occupied by each molecule of the substance while on the surface. Then, since the adsorbed film is in equilibrium with the surrounding gas, we have[1]

$$\alpha_1\mu_1 = \nu_1\theta_1^n. \tag{17}$$

Now the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from m adjacent spaces. In case of a dissociation m will be equal to unity. If ω represents the velocity of the chemical change, we have

$$\omega = \nu_2\theta_1^m. \tag{18}$$

Combining these two equations gives

$$\omega = \nu_2\left(\frac{\alpha_1\mu_1}{\nu_1}\right)^{m/n}. \tag{19}$$

The velocity of the reaction thus varies with the m/nth power of the pressure (μ) of the gas. In the case of the dissociation of hydrogen molecules by a heated wire, we have $m = 1$ and $n = 2$, so that the velocity at which the gas is dissociated is proportional to the *square root* of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire, however, takes place in proportion to the *square* of the pressure of the atomic hydrogen. It has been shown previously that these conclusions are in accord with experiments.

Bodenstein and Ohlmer[2] mention that the velocity of the reaction between carbon monoxide and oxygen in presence of heated crystalline quartz is proportional to the pressure of the carbon monoxide and to the *square root* of the pressure of oxygen.

Now if we assume that each carbon monoxide molecule occupies one elementary space while each oxygen molecule occupies two (i.e., is present on the surface in the form of atoms), we obtain

$$\begin{aligned} \alpha_1\mu_1 &= \nu_1\theta_1 \\ \alpha_2\mu_2 &= \nu_2\theta_2^2 \\ \omega &= \nu_3\theta_1\theta_2 \end{aligned} \tag{20}$$

where the subscript 1 refers to CO, 2 refers to O_2 and 3 refers to CO_2.

---

[1] This equation becomes identical with Equation 14 only when $n = 1$ and $\theta = 1$. It is thus seen that the theory of adsorption which led to Equation 16 does not apply to the case where a molecule occupies more than one elementary space. Equation 17 shows that when $n = 2$, the amount of gas adsorbed is proportional to the square root of the pressure, even at very low pressures.

The equations that follow (19), (21), etc., may be derived in several different ways (see *J. Am. Chem. Soc.* **38**, 1149 (1916)) by making different kinds of assumptions. By experiment it will be possible to determine which set of assumptions correspond with the facts.

[2] *Z. physik. Chem.* **53**, 175 (1905).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

These equations give

$$\omega = k\mu_1 \sqrt{\mu_2} \tag{21}$$

where k is a constant involving α_1, α_2, ν_1, etc. Thus the relation found by Bodenstein and Ohlmer follows directly from the assumption that the oxygen adsorbed on the surface is present as separate atoms.

It has been found by Bodenstein and Kranendeck (p. 99, Nernst Festschrift) that the rate of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure. It will be shown in a subsequent paper that this fact is readily explainable by assumptions analogous to the above.

Freundlich and Bjercke[1] have recently found that the rate of oxidation of phenyl-thiourea by oxygen in contact with blood charcoal is proportional to the square root of the concentration of oxygen.

It should be noted that the velocity of gas reactions is frequently proportional to the square root of the pressure, whereas according to the law of mass action, we should expect velocities proportional to some integral power of the pressure. The above theory of heterogeneous reactions offers a simple explanation of these fractional exponents. According to the Bodenstein-Fink theory of heterogeneous reactions, such square-root relations are to be explained by diffusion through films whose thickness varies in proportion to the square-root of the pressure. There is definite experimental evidence in the case of the dissociation of hydrogen (which gives a square root relation) that the adsorbed film covers only a very small fraction of the surface with a layer one atom deep. Hence the Bodenstein-Fink theory cannot possibly explain this case. It is very probable that such square root relations are never caused by diffusion through adsorbed films.

Second Case. Surface Nearly Completely Covered

Let us consider a reaction in which two gases are in contact with a solid body. One of the gases, which we shall designate by the subscript 1, is present in such quantity and evaporates so slowly from the surface that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas, 2, undergoes a chemical change when its molecules come in contact with the uncovered surface. This reaction may be of several kinds. For instance, the gas molecules condensing in vacant spaces may dissociate, may react with the underlying solid, or may react with the adsorbed gas in adjacent spaces. The rate at which the first gas will condense is $\alpha_1\theta^n\mu_1$, where n is the number of elementary spaces occupied by each molecule which condenses. The rate of evaporation will be constant ν_1, since the surface is nearly covered. Therefore, for equilibrium

$$\alpha_1\theta^n\mu_1 = \nu_1. \tag{22}$$

[1] *Z. physik. Chem.* **91**, 1 (1916).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The rate at which the second gas will enter into reaction will usually be proportional to $\theta\mu$. It is quite possible, however, in some cases that θ may have any integral or even fractional exponent. We thus obtain for the rate of reaction

$$\omega = \nu_2 \theta \mu_2, \tag{23}$$

Combining these equations we find

$$\omega = \nu_2 \mu_2 \left(\frac{\nu_1}{\alpha_1 \mu_1} \right)^{1/n}. \tag{24}$$

The velocity of the reaction is thus proportional to the pressure of gas 2, and *inversely proportional to the* nth *root* of the pressure of gas 1.

Now this is a relation which has been found to hold for a very great number of heterogeneous reactions in which the velocity is influenced by catalytic poisons. A few of these will be briefly mentioned.

Fink[1] found in the case of the reaction (in contact with platinum)

$$2SO_2 + O_2 = 2SO_3$$

that the velocity is proportional to the pressure of SO_2 and inversely proportional to the square root of the pressure of SO_3. This relation follows directly from Equation (24) if we place $n = 2$. We may thus conclude that the platinum surface was practically completely covered by a layer of adsorbed SO_3 in which each molecule of SO_3 required two elementary spaces for its condensation. Fink actually measured the amount of adsorbed SO_3 and found it to be of the order of magnitude of a single layer of molecules. According to the Fink-Bodenstein theory, the amount of adsorbed SO_3 in these experiments should have been proportional to the square root of the SO_3 pressure, whereas according to the above theory the amount adsorbed should have been practically independent of the pressure (saturation). It is, however, obvious that a film one molecule thick (as found by Fink) cannot have a *thickness* which varies in proportion to the square root of the pressures over a wide range.

Bodenstein and Ohlmer found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of oxygen and inversely proportional to the pressure of carbon monoxide. Evidently here $n = 1$ so that each molecule of carbon monoxide occupies only one elementary space.

The writer has found[2] that the same relation holds when these gases react with each other at very low pressures in contact with platinum. It was also found[3] that in the catalysis of oxygen-hydrogen mixtures by a plati-

---

[1] Dissertation, Leipzig, 1907; see also Bodenstein and Fink, *Z. physik. Chem.* **60**, 1 (1907).

[2] *J. Am. Chem. Soc.* **37**, 1162 (1915).

[3] More recent experiments show that this is not the usual manner in which hydrogen and oxygen react in contact with platinum even at low pressures. The factors which cause the above type of reaction have not yet been determined with certainty.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

num wire, the velocity is proportional to the pressure of oxygen and inversely proportional to that of the hydrogen.

An interesting application of this theory arises in connection with enzyme action. The velocity of many of these reactions varies in accordance with Schutz's rule.[1] Consider a reaction in which a substance A is converted into B by the action of an enzyme. Let x be the amount of B formed in the time t, assuming that the substance B is absent when $t = 0$. Let E be the amount of enzyme present. Then according to Schutz's rule

$$x = k\sqrt{\mathrm{E}t}. \tag{25}$$

Thus the amount of B formed is independent of the concentration of A, but is proportional to $\sqrt{\mathrm{E}t}$.

By squaring and differentiating (25) we obtain, if E remains constant

$$\frac{dx}{dt} = {}^1/_2 k^2 \frac{\mathrm{E}}{x}. \tag{26}$$

Thus another way of stating Schutz's rule is to say that the velocity of the reaction is proportional to the amount of enzyme, is inversely proportional to the amount of B formed, and is independent of the amount of A.

It is generally recognized that enzymes are colloids on the surfaces of which reactions occur. We may thus interpret Schutz's rule as an indication that the product B of the reaction is adsorbed on the surface of the colloidal particles forming a layer one molecule deep nearly completely covering the surface. By comparing Equations 26 and 24 we see that $n = 1$ from which we conclude that each adsorbed molecule occupies only one elementary space. The reaction thus takes place only on that fraction of the surface which is not covered by molecules of B.

By Equation 24 we should expect the velocity of the reaction to be proportional to the concentration of A, but according to Schutz's rule the velocity is independent of this concentration. This seems somewhat difficult to explain. It is, perhaps, possible that molecules of A are adsorbed over practically all the surface not occupied by B, and that molecules of B are able to *displace* molecules of A thus adsorbed. Let θ_a and θ_b be the fractions of the surface covered by A and B, respectively. Then according to the above hypothesis, we would have

$$a_b \theta_a \mu_b = \nu_b \theta_b. \tag{27}$$

$$\omega = \nu_a \theta_a. \tag{28}$$

Since θ_b is nearly equal to unity, we thus have

$$\omega = \left(\frac{\nu_a \nu_b}{a_b}\right)\frac{1}{\mu_b}, \tag{29}$$

which is of exactly the same form as (26) and is thus equivalent to Schutz's rule.

[1] See Euler, *Allegemeine Chemie der Enzyme*, pp. 125, 106 and 113.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Summary

1. The work of the Braggs on crystal structure is reviewed from the viewpoint of the chemist and the relation of this work to theories of chemical constitution such as those of Werner, Stark, J. J. Thomson, and Lewis, is discussed in detail.

2. It is concluded that the substances whose structures have thus far been studied by the X-ray spectrograph are not representative of compounds in general. Only polar compounds have been studied.

3. Solid polar compounds are, in general, built up of atoms bound together by secondary or residual valence. The whole crystal must be regarded as a single molecule.

4. Solid nonpolar compounds consist in general of "Group Molecules" in which the atoms are usually held together by primary valence. These group molecules in turn are bound together by secondary valence to form a large "Crystal Molecule," which includes the whole solid mass.

5. There is no present justification for dividing interatomic (or intermolecular) forces into *physical* and *chemical* forces. It is much more profitable to consider all such forces as strictly chemical in nature. Evaporation, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena. The object of this paper is largely to show that *chemical knowledge already available* is directly applicable to the study of these phenomena.

6. From a consideration of such properties as specific heat, compressibility, coefficient of expansion, etc., it is concluded that collisions do not take place between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces.

7. The "time of relaxation" of the atoms of solids is calculated approximately from the heat conductivity and is found to be of the order of 10^{-14} to 10^{-7} seconds. An independent method by which the "time of relaxation" can be calculated from the rate of evaporation of a substance in vacuum, gives substantially similar results. Thus the time necessary for an atom of a solid to reach thermal equilibrium with its neighbors is very small compared to the time necessary to make a single oscillation about an equilibrium position. The "oscillations" are thus extremely strongly damped.

8. Since solid substances in general are held together by secondary rather than primary valence, there are few limitations to the number of compounds that can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the ordinary rules of valence. Metallic compounds, minerals, solid solutions and glasses are discussed from this point of view.

9. By considerations based largely on the compressibility, it is concluded that the attractive forces between atoms usually reach a maximum intensity

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

when the distance between adjacent atoms in solids is increased by about 0.6×10^{-8} cm (10–30% of the normal distance between atoms).

10. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption.

11. Because of the small time of relaxation and because an atom approaching the surface is attracted by many, but later is repelled by few atoms, it follows that the surfaces of solids are almost wholly inelastic in regard to collisions of molecules impinging on the surface. There is also a great deal of experimental evidence of this inelasticity. As a result, nearly every molecule or atom striking a solid surface condenses no matter what the temperature may be. While condensed it is held to the surface by forces quite similar to those holding solids together (either primary or secondary valence). At high temperatures evaporation may take place almost immediately after condensation, but at lower temperatures, the condensed atom or molecule may remain indefinitely.

12. The phenomena of condensation and evaporation (sublimation) of solids is discussed at some length. In general, the rate of evaporation (m) of a substance in a high vacuum is related to the pressure (p) of the saturated vapor by the equation

$$m = \sqrt{\frac{M}{2\pi RT}} p.$$

Red phosphorus and some other substances probably form exceptions to this rule.

13. The mechanism of the dissociation of a solid, such as $CaCO_3$ is discussed. It is shown that when, according to the phase rule, separate phases of constant composition are present, the reaction must take place exclusively at the boundaries of these phases. This kinetic interpretation of the phase rule indicates clearly the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that hydrated crystals frequently fail to effloresce unless scratched and for the fact that thoroughly dehydrated substances often absorb moisture with great difficulty.

14. Adsorption is a direct consequence of the time lag between the condensation and the subsequent evaporation of molecules. The adsorbed substance may be held to the surface either by secondary or primary valence. In either case it is profitable to regard the phenomena as chemical in nature. A large number of experimental results are given which prove conclusively

Digitized by Google Original from UNIVERSITY OF MICHIGAN

that adsorption is very frequently the result of the strongest kind of chemical union (primary valence) between the atoms of the adsorbed substance and the atoms of the solid.

15. It is shown that the action of a typical catalytic poison depends on the formation of a very stable film one atom deep over the surface of the catalyzer. The chemical activity of any solid surface depends upon the nature of, the arrangement of, and the spacing of the *atoms* forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it (either thermionic or photoelectric emission).

16. A brief quantitative development of this theory of heterogeneous reactions is given. A "law of surface action" analogous to but different from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichinstein's "Constant Sum Hypothesis". An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic *chemical* phenomena. It depends particularly upon the *shapes* of the group molecules and upon the relative intensities of the chemical activity of *different portions* of the molecules. A method will be described (together with experimental data) by which the *cross sections*, *lengths* and other dimensions of group molecules of liquids may be determined.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS

PART II. LIQUIDS[1]

Journal of the American Chemical Society
Vol. XXXIX, No. 9, 1848, September (1917).

IN PART I[2], reasons have been given for believing that all the forces acting between atoms (or group molecules) in solid bodies are fundamentally similar in character and are of the nature of so-called chemical forces. Thus, evapora-

---

[1] The fundamental idea of the orientation of group molecules in the surfaces and in the interior of liquids as a factor of vital importance in surface tension and related phenomena, occurred to me in nearly its present form in June and July, 1916. During August surface-tension data for over 250 substances were tabulated and studied. Work on oil films began in June. As a result of this extensive work, clear ideas were obtained as to the orientation of molecules in the surfaces of liquids and the relation between the total energy $\gamma_0 = \gamma - T\, d\gamma/dT$ and the chemical constitution of such substances as benzene and its disubstitution products.

An account of this work was given in some detail in a paper read at the New York meeting of th American Chemical Society in September, 1916, and a short abstract was published in *Met. Chem. Eng.* **15**, 468 (1916). In this abstract only the more important conclusions were outlined, while the large amount of experimental data upon which these conclusions were based were, unfortunately, not given.

On Oct. 27th, at the Cleveland meeting of the American Physical Society, I described the mechanism of surface-tension phenomena, and presented the data for γ_0 for about 100 typical substances, and pointed out in detail the arrangements of molecules of benzene substitution products, especially indicating the effects characteristic of the ortho, meta and para positions of a number of active and inactive groups. The bearing of this work on the hypothesis of the association of liquids was also pointed out.

Since this time I have found that Prof. W. D. Harkins has been developing an essentially similar theory of surface-tension phenomena. He has recently published two papers on this subject in *J. Am. Chem. Soc.* **39**, 354 and 541 (1917).

Nearly all the data in the second of these papers (except of course the new experimental data presented), had been worked over by me during the summer of 1916 and it was my intention to publish them together with the material now given in the present paper. Dr. Harkness, however, kindly sent me advance manuscript of his papers, and I have therefore been able to avoid duplication of his work. Harkins had expected that his two articles would appear simultaneously, and, as an unfortunate result he failed in his first article to mention my prior publication. In his second paper he refers to my work, but, by an oversight, fails to refer to the publication of my general results in *Met. Chem. Eng.*, although in the latter part of his paper (page 584) he refers to this abstract in a footnote in which he points out that his conclusions regarding the orientation of the benzene molecules in the surface are the same as mine.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

tion, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena.

Before proceeding with the application of this viewpoint to a consideration of the structure of liquids it will be profitable to examine more closely

---

Under these circumstances it is desirable to quote a part of the abstract in *Met. Chem. Eng.* **15**, 469 (1916), as follows:

"A theory of surface tension is now proposed in which the structure of the *surface layer of atoms* is regarded as the principal factor in determining the surface tension (or rather surface energy) of liquids. This theory is supported in the most remarkable way by all available published data on the tension of organic liquids.

"According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface layer. By 'active portion' of a molecule is meant a portion which is characterized by a strong stray field (residual valence). Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum.

"The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

"In liquid hydrocarbons of the paraffin series the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains from the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact, the surface energy of all these many different substances from hexane to molten paraffin, have substantially the same surface energy, namely, 46 to 48 ergs per sq. cm, although the molecular weights differ very greatly.

"If, now, we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies* are *practically identical with those of the hydrocarbons*. The reason for this is that the surface layer in both cases consists of CH_3 groups.

"With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy.

"Particularly interesting relations are found with benzene derivatives.

"In benzene, itself, the group molecules arrange themselves so that the benzene rings lie flat on the surface, since the flat sides of these rings are the least active portions of the molecules. The surface energy of benzene is about 65 ergs per square cm.

"If, now, an active group, such as OH, is substituted for one of the hydrogens in the benzene (forming phenol or carbolic acid) this group is drawn into the body of the liquid *tilting the benzene ring up on edge* and raising the surface energy to about 74 ergs per sq. cm, which corresponds to the activity of the perimeter of the benzene ring. Thus *any active group* strong enough to tilt the ring up on edge raises the surface energy to about 75. Two active groups side by side (ortho position) gave no greater effect than one. But two active groups opposite one another (para position) cannot both go wholly below the surface, so that the surface energy then becomes abnormally large (about 85 in case of *p*-nitrophenol). The substitution of methyl or ethyl groups in the benzene ring lowers the surface energy except where an active group in an adjacent position draws these groups below the surface.

"Some of the best evidence in support of the new theory is derived from experiments on thin films of oil on water or mercury. Oleic acid on water forms a film one molecule deep, in which

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

than heretofore the distinctions between this theory and the more usually accepted theory, according to which the above listed phenomena are manifestations of physical forces.

"Physical" versus "Chemical" Forces

When considering the action of forces between discreet particles in space, the physicist usually makes the simplifying assumption that each particle attracts or repels each other particle with a force which varies according to a function of the distance between the particles. Newton's inverse square law for gravitational attraction and Coulomb's law for the attraction or repulsion between electric charges, are familiar examples of such relations. Maxwell calculated the effect of temperature on the viscosity of gases on the assumption that molecules attract one another inversely as the square and repel inversely as the fifth power of their distance. Sutherland found that a formula in better agreement with the facts could be derived by assuming the molecules to be rigid spheres attracting one another with a force inversely as the n^{th} power of the distance.

---

the hydrocarbon chains stand vertically on the water surface with the COOH groups in contact with the water.

"Acetic acid is readily soluble in water because the COOH group has a strong secondary valence by which it combines with water. Oleic acid is not soluble because the affinity of the hydrocarbon chains for water is less than their affinity for each other. When oleic acid is placed on water the acid spreads upon the water because by so doing *the COOH can dissolve in the water* without separating the hydrocarbon chains from each other.

"When the surface on which the acid spreads is sufficiently large the double bond in the hydrocarbon chain is also drawn down on to the water surface, so that the area occupied is much greater than in the case of the saturated fatty acids.

"Oils which do not contain active groups, as for example pure paraffin oil, do not spread upon the surface of water."

[2] *J. Am. Chem. Soc.* **38**, 2221 (1916). On page 9 of Part I the relationship between Werner's theory and the work on crystal structure was pointed out. The writer regrets that at that time he was not aware that P. Pfeiffer (*Z. anorg. Chem.* **92**, 376 (1915)) has previously published a short paper discussing crystal structure from the viewpoint of Werner's theory. This has since been called to the writer's attention by Dr. G. McP. Smith. Even before the publication of Pfeiffer's paper, however, the writer had pointed out the application of Werner's theory to crystal structure in a paper read before the American Physical Society at Washington, D. C., on April 24, 1915 and an abstract of this paper was published (*Phys. Rev.* **6**, 79 (1915)) a couple of weeks before Pfeiffer's article. The abstract contains the following reference to this subject: "Bragg has shown that the atoms of crystals are arranged according to a space lattice, the identity of the molecules being lost. The forces acting between the atoms are thus chemical forces. In the case of diamond, the tetravalent character of carbon is manifest from the structure, but in most cases the valency appears to be *divided* between several atoms. Thus, in sodium chloride the single valency of the sodium atom is divided between six chlorine atoms. There is a close connection between this theory and Werner's theory of valence."

R. B. Sosman, in a paper (*J. Ind. Eng. Chem.* **8**, 985 (1916)) which appeared nearly simultaneously with Part I of the present paper, has discussed the structure of silicates and other crystalline compounds from a viewpoint almost identical with that developed by the present writer.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Van der Waals' equation of state for gases is based on the assumption that molecules attract one another according to some function involving only the distance between them. This method of derivation tacitly assumes that the forces do not depend on the orientation of the molecules, and further assumes that the force acting between any two molecules is not influenced by the proximity of other molecules.

J. E. Mills, in a series of papers on the subject of "Molecular Attraction",[1] has advanced the theory that the only force acting between molecules in gases and liquids is an attractive force which varies inversely as the square of the distance between molecules.

Bakker[2] has developed a theory of surface tension based on the assumption that the molecules of liquids attract one another according to an inverse exponential function of the distance. A somewhat similar theory of adsorption has been developed by Eucken.[3]

These are only a few examples of the cases in which the forces between the molecules have been considered to be radial forces which vary solely as a function of the distance between molecules. In all the cases cited above the investigator has considered the phenomena to be physical in nature.

The chemist, on the other hand, in studying the properties of matter, usually employs totally different methods. He is often most interested in the equalitative aspects of a problem, and the quantitative relationships sought are usually limited to those deducible from the law of multiple combining proportions, the law of mass action or the principles of thermodynamics. When the chemist does consider the forces acting between atoms or molecules, he does not look upon these as forces of attraction between the centers of the molecules, but he thinks rather of the specific nature of the atoms forming the molecules and the manner in which these atoms are already combined with each other. He thinks of molecules as complex structures, the different portions of which can act entirely differently towards any given reagent. Furthermore, he considers that the forces involved in chemical changes have a range of action which is usually much less than the diameter of a molecule and perhaps even less than that of an atom.

Gurvich[4] distinguishes physical and chemical forces as follows:

"I. *Physical Force of Attraction*:

(*a*) is not specific;

(*b*) has unlimited range of action;

(*c*) its action on a given mass is independent of the presence of other masses;

(*d*) it does not act atomistically; that is, it acts on masses as a whole and not along definite directions."

---

[1] A dozen or more papers on this subject have appeared in the *J. Phys. Chem.*

[2] *Z. physik Chem.* **89**, 1 (1915).

[3] *Verh. deut. physik. Ges.* **16**, 345 (1914).

[4] *Z. physik. Chem.* **87**, 323 (1914).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

"II. *Chemical Force of Attraction* (*Affinity*):

(*a*) is specific;

(*b*) its range of action is limited, probably to *atomic* distances;

(*c*) its action upon a given mass depends upon whether or not the force is already practically 'saturated' by other masses;

(*d*) it acts atomistically; that is, discontinuously in a few single rays or directions."

Gurvich considers that the forces involved in adsorption phenomena are not to be classed in either of these groups, but should rather be regarded as physico-chemical forces, as follows:

"III. *Physico-chemical Force of Attraction*:

(*a*) is specific;

(*b*) its range of action is limited to molecular distances;

(*c*) its action upon a given mass is dependent on the presence of other masses;

(*d*) it is not atomistic, but acts as a whole without division into separate rays or directions".

The point of view developed in the present paper leads us to the following conclusions:

A. Forces of the type which Gurvich has called Physical Forces do not play any important part in the structure of matter. The best examples of the physical forces are gravitation and the forces between electrically charged bodies. Gravitation is much too small a force to be of influence in holding atoms and molecules together. In all ordinary matter the negative and positive electricity are so uniformly distributed throughout the mass that the effective range of these electric forces is only of atomic dimensions.

B. *All* the interatomic and intermolecular forces involved in the structure of matter are chemical forces; that is, they are of the same nature as the forces that the chemist has been studying in the past. In general, these forces are of two kinds: those represented by primary and those represented by secondary valence. Adopting a scheme similar to that proposed by Gurvich, the characteristics of these forces are:

"IV. *Chemical Force* (*Primary Valence*):

(*a*) is very specific;

(*b*) its range of action is limited to distances comparable to the diameters of atoms;

When several atoms are combined together by primary valence, however, certain effects may be transmitted from atom to atom over distances several times the diameter of atoms;

(*c*) its action depends entirely upon the degree of saturation of the atoms;

(*d*) it acts atomistically, in definite directions;"

"V. *Chemical Force* (*Secondary Valence*):

(*a*) is moderately specific;

(*b*) its range of action in limited to atomic distances except where transmitted from atom to atom. The ranges of primary and secondary valences do not seem markedly different;

(*c*) its action depends on the presence of neighboring atoms (Werner's cooridnation number), but not in such a definite way as in the case of primary valence;

(*d*) it acts only between adjacent atoms, but usually not in directions radiating out from single atoms."

In the great majority of cases, as has been shown by Werner, the distinctions between primary and secondary valence are well defined. Many cases of tran-

Digitized by Google Original from UNIVERSITY OF MICHIGAN

sition occur between the two, however, so that hard and fast rules should not be adopted.

The theory of valence recently advanced by G. N. Lewis[1] seems to offer by far the most satisfactory picture of the mechanism of chemical combination that has yet been suggested. According to this theory the electrons in the outer shells of atoms tend to arrange themselves in groups of eight. There is also a very marked tendency for the electrons to group in pairs around positive charges. Thus, the stability of the hydrogen molecule and the helium atom is due to the existence of a stable pair of electrons. The neon atom contains an inner pair of electrons, with a stable group of eight electrons in the outer shell.

A carbon atom has four electrons in the outer shell. In the formation of methane the four electrons from four hydrogen atoms complete the group of eight. These eight electrons gather into four pairs, each of which holds one of the hydrogen nuclei in about the same way as the two nuclei are held together in a hydrogen molecule. In the molecule thus formed we cannot say that positively charged hydrogen ions are held electrostatically by a carbon atom with four negative charges. The eight electrons belong as much to the hydrogen nuclei as to the carbon atom. The chemical union is brought about by the electrons ***held in common*** by all the atoms. Thus, methane is a non-polar substance.

Similarly, the structure of carbon tetrachloride is accounted for and it is readily seen why it too, does not have a polar character.

When sodium and chlorine combine, the single outer electron of the sodium atom, together with the seven electrons in the outer shell of the chlorine atom form the stable group of eight. In this case we have more reason to look upon the resulting compound as consisting of a negatively charged chlorine ion held by electrostatic forces to a positively charged sodium ion. Since the chlorine ion and the chlorine atom have radically different structures, however, it is not a useful conception to regard a chlorine ion as a charged chlorine atom.

This viewpoint leads us to a much clearer conception of the nature of primary and secondary valences.

Primary valence is the result of the tendency of the electrons to form groups of two or eight[2]. In the strongly polar compounds, electrons are transferred from the outer shells of the electropositive atoms to the outer shells of the negative atoms, in order to complete the stable groups of electrons. The primary valence relationships are dependent on the number of electrons that can be so transferred. In non-polar compounds, such as typical organic substances, a pair of electrons, held in common by two adjacent atoms, constitutes what we have usually represented by the single bond (primary valence).

---

[1] *J. Am. Chem. Soc.* **38**, 762 (1916).

[2] For the elements after the first two short periods it is evident that the electrons in the outer shell tend to arrange themselves in other ways than in groups of eight. We may expect, however, that Lewis' theory will soon be extended to cover these elements. Kossel's theory has made some progress in this direction.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

When two or more atoms are thus combined by pairs of electrons held in common, there are still stray fields of force due to the electrons forming the outer shells of the atoms. Secondary valence is the result of these stray fields. The coordination number represents the number of groups which can arrange themselves in space around a given group. As was shown in Part I, a solid or liquid body (as, for example, a metal,) may be built up of atoms held together exclusively by secondary valence.

From this viewpoint both primary and secondary valences are active in the formation of a crystal of sodium chloride. The transfer of the electron from the shell of the sodium atom to that of the chlorine atom involves primary valence. The two charged groups of electrons are then held together by their electrostatic fields to form the crystal (secondary valence). We thus see how, in a crystal, the arrangement of the atoms in no wise suggests the primary valence of the atoms, yet the chemical composition is in full accord with the ordinary rules of valence.

Not only Lewis's theory, but other recent theories of chemical valence, such as those of Stark, J. J. Thomson, and Kossel[1], enable us to draw similar distinctions between primary and secondary valence.

Nothing definite is known regarding the forces acting on electrons inside of atoms. There seems to be increasing evidence that the electrons in atoms are not revolving in orbits around the positive nuclei, but should rather be regarded as stationary except when disturbed from their equilibrium positions by external forces. It may be, however, that a magnetic field (Parson's theory) is to be associated even with stationary electrons in the atom. If this viewpoint is correct, we can no longer fall back on the convenient centrifugal force to explain why the electrons do not fall into the positive nucleus.

The writer believes with G. N. Lewis that Coulomb's law fails at short distances. From the internal structure of atoms we may, however, draw certain conclusions as to the nature of this failure. Since the electrons remain apart from the nucleus, it is evident that positive and negative charges repel one another when brought sufficiently near. The tendency of electrons to form stable pairs in atoms seems to indicate that two negative electrons (at least under the influence of neighboring positive charges) attract one another when close together. Furthermore, it seems to be a reasonable hypothesis that an alpha particle consists of *two* hydrogen nuclei (positive electrons) which nearly coincide and therefore, according to the electromagnetic theory, possess nearly four times the mass of a single hydrogen nucleus. In this case we would also conclude that two positive electrons, when brought sufficiently close together, attract one another and form the very stable alpha particle.

From the viewpoint of these hypotheses, chemical combination by primary valence is the result of those as yet mysterious forces which cause electrons in atoms to be attracted together into pairs, or groups of eight.

[1] Ann Phys. [4] **49**, 229 (1916).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The resulting molecules, or group molecules, have electrons arranged in definite ways in their outer shells. Thus, their surfaces should be looked upon as containing a large number of electric doublets and probably also magnetic doublets. When two molecules are brought close together, the doublets of one attract the doublets of the other and result in the attraction between the two molecules associated with the secondary valence.

It is evident, however, if we are to regard these secondary valence forces as being due to doublets, that we should not expect the force between the molecules to vary simply as a function of the distance or to show other characteristics of the Physical Forces (1). For example, let us consider the case of simple doublets such as bar magnets. One magnet attracts another with a force that depends primarily on the relative orientation of the two magnets. If two magnets come close together so that the north pole of one comes close to the south pole of the other the action of these magnets on a third has in general been greatly reduced. On the other hand, if the two magnets are placed end to end the attraction for a third may be greatly increased. These relationships are more nearly of the kind that we expect among chemical forces between atoms, rather than among physical forces such as those described by Gurvich. Thus from purely theoretical grounds, if inter-atomic forces are due to the presence of doublets, we conclude that all forces involved in cohesion, surface tension, etc., should come under the division of "Chemical Forces".

Nevertheless, the assumptions that have been made by van der Waals, Eucken, Mills, Bakker, etc., in their studies of the so-called physical properties of matter are not wholly unjustifiable. When molecules are separated by distances large compared to their diameters, under conditions such that all possible orientations occur with nearly equal probability, then it is evident that the *average force* between molecules will, for practical purposes, be a function solely of the distance between them. When, however, the molecules approach so closely that they exert a marked orienting effect upon each other, then it is no longer justifiable, any more than it was in the case of the bar magnets, to consider that the forces vary as a function merely of the distance.

The errors resulting from the assumption that the force varies solely with the distance become less important when we are dealing with atoms in which there are many doublets on the surfaces, and these doublets are uniformly distributed over the surface and are of small intensity.

In the case of the so-called permanent gases these conditions are fairly well fulfilled; also in so-called non-associated liquids there is a rough approximation to these conditions, so that certain useful results may be obtained by means of the simplifying assumption that the force varies as a function of the distance. However, such results should only be expected to hold in the case of molecules having *symmetrical* force fields and only when the distances between molecules is sufficiently great.

In the majority of cases, such simplifying assumptions are not justifiable

Digitized by Google Original from UNIVERSITY OF MICHIGAN

and for this reason the formulas derived often fail completely when applied to certain substances or over too wide a range of conditions. It will be shown in the present paper (Part III) that the so-called associated liquids are merely substances which conform particularly badly with the customary simplifying assumptions. From the viewpoint developed in these pages such substances are in no wise to be regarded as abnormal. In other words, if we regard all the "physical properties" as resulting from chemical forces we are able to derive relationships which apply equally well to "normal" and to "associated" liquids.

The point that I wish to emphasize especially in the present paper is that such phenomena as cohesion, evaporation, crystallization, adsorption, surface tension, viscosity, etc., apparently do not involve any interatomic or "intermolecular" forces other than the two kinds of force (IV and V) already familiar to the chemist.

The Relations between Solids and Liquids

The differences between the properties of solids and liquids are much smaller than those between liquids and gases. The change in density in passing from the solid to the liquid state is insignificant in comparison with the change that occurs in passing from the liquid state to that of the gaseous (at ordinary pressures). Similarly, the compressibilities, coefficients of expansion, specific heats, refractive indices and other optical properties, dielectric constants, and thermal conductivities of solids and liquids do not differ very materially in comparison with those of gases. For example, the similarity of solid and liquid mercury is in marked contrast to the great differences between liquid and gaseous mercury. In the gaseous state the mercury is colorless, transparent and is a non-conductor of electricity, but the optical and electrical properties of solid and liquid mercury differ only slightly.

In fact, the only essential differences between liquids and solids seem to lie in the mobility of liquids and in those properties which are directly dependent on mobility. As a result of this mobility, the definite lattice arrangement of the atoms of solids gives way to the irregular arrangements characteristic of liquids. The viscosity and the shearing elasticity of liquids are of course totally different from those of solids.

Surface tension is a property which we usually associate only with liquids. There is no doubt but that solids possess surface energy and that the only reason that this does not manifest itself more clearly as a surface tension is that the solids do not possess sufficient mobility.

When a liquid shows electrolytic conductivity then the conductivity of the corresponding solid is usually much smaller because of the decreased mobility of the ions. But where the conductivity is metallic there is ordinarily no great difference between the conductivities in the two states.

From these considerations, it is evident that the forces involved in the structures of liquids are not essentially different from those of solids. We may

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

also reach this conclusion (as was done in Part I), by arguing that amorphous and crystalline solids differ only as regards the regularity of the arrangement of their atoms, and by then considering that liquids may be obtained by a continuous process from amorphous solids, if we merely increase the mobility by raising the temperature.

If the forces holding solid bodies together are chemical forces represented by primary and secondary valence, then there is every reason for believing that chemical forces are also responsible for holding the atoms and group molecules of liquids together. Conversely, all the experimental evidence we find regarding the chemical nature of the forces within liquids may be considered as additional evidence in favor of a similar theory for solids.

The mobility of a liquid is thus due to a shifting of the relative positions of atoms which are all chemically combined with each other.

This mobility of atoms within the chemical molecule is nothing more than the familar phenomenon of tautomerism. In the field of organic chemistry, this phenomenon has attracted considerable attention because it seems to form such a marked exception to the behavior of most organic compounds. As Lewis has pointed, however, tautomerism is an almost universal characteristic of inorganic substances (in the liquid state).

It seems probable that tautomerism occurs much more frequently in secondary valence unions than in those involving primary valency. It therefore occurs at the boundaries of the group molecules of organic substances rather than within these groups. The only solid body which seems to be held together exclusively by primary valence is the diamond (and presumably other forms of carbon), and this substance has never been obtained in the liquid state.

According to this viewpoint the viscosity of liquids depends upon the frequency with which tautomeric changes occur between the atoms or at the boundaries of the group molecules. This aspect of the theory will be considered again under the heading, "Viscosity".

Oil Films on Water

When a very small quantity of an oil, such as olive oil, is placed upon a large clean surface of water, the oil spreads rapidly upon the water surface until a definite area has been covered and then the oil shows little or no tendency to spread further. The writer's attention was first called to this remarkable phenomenon by reading an article by A. Marcelin[1] on the "Minimum Thickness of Oil Films on Water".

Miss A. Pockels[2] showed that very small amounts of oil on the surface of water have no appreciable effect on the surface tension, but that the surface tension begins to *decrease suddenly* when the amount of oil per unit area is increased beyond a certain sharp limit.

---

[1] *Ann. Phys.* **1**, 19 (1914).

[2] *Nature* **43**, 437 (1891).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Lord Rayleigh[1] repeated these experiments and clearly pointed out the importance of the phenomena, in the explanation of the mechanism of surface tension. In Miss Pockel's and in Rayleigh's experiments a very small amount of oil is placed on water contained in a long narrow trough. The oil is prevented from spreading over the whole surface by barriers consisting of strips of glass placed across the tray and resting on the edges. By sliding these barriers along the tray the area of water, on which the given quantity of oil may spread, can be varied at will. Rayleigh measured the surface tension of the contaminated water between the barriers by Wilhelmy's method; that is, a thin blade was

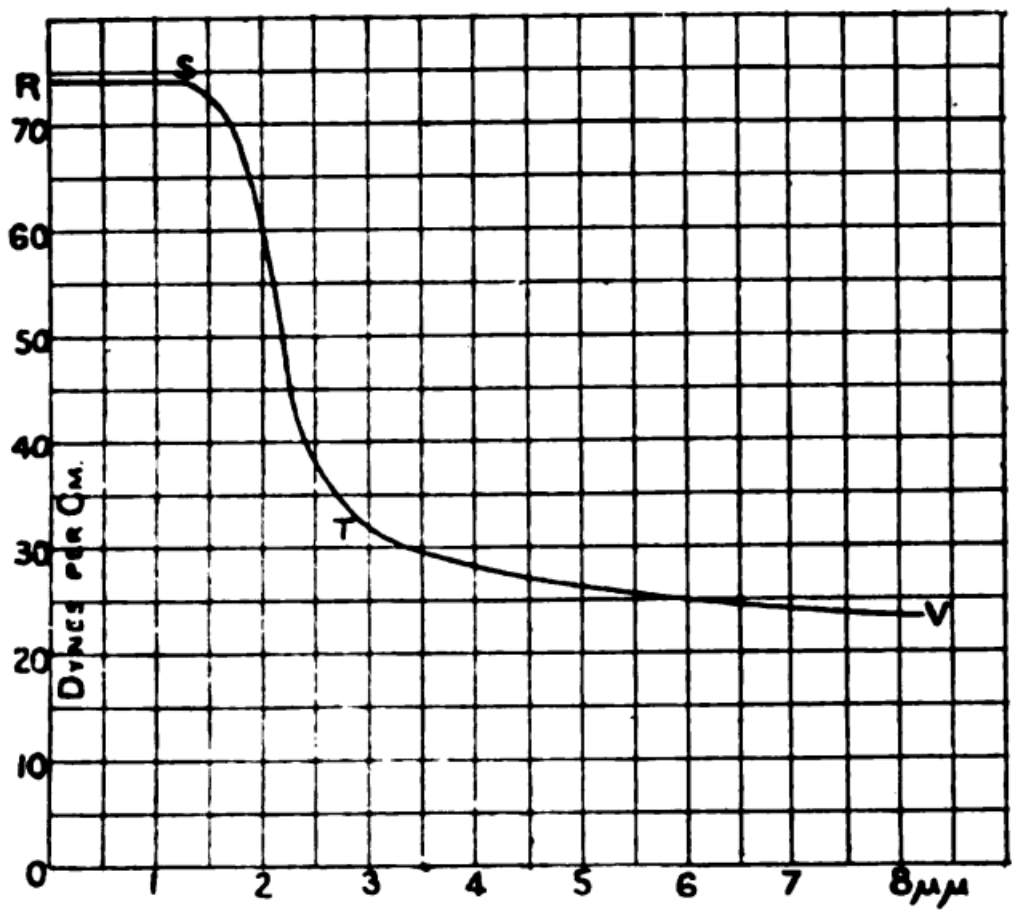


FIG. 1.

mounted in a balance, its plane being vertical and its lower horizontal edge dipping under the surface of the water. As the "thickness" of the oil film was varied by shifting the position of one of the barriers, the surface tension changed in the manner shown in Fig. 1[2], which represents a curve obtained with a film of castor-oil.

"Now this is only a moderate multiple of the supposed diameter of a gaseous molecule, and perhaps scarcely exceeds at all the diameter to be attributed to a molecule of oil. It is obvious therefore that the present phenomena lie entirely outside the scope of a theory such as Laplace's in which matter is regarded as continuous, and that an explanation requires a direct consideration of molecules.

"If we begin by supposing the number of molecules of oil upon a water surface to be small enough, not only will every molecule be able to approach the water as closely as it desires, but any repulsion between molecules will have exhausted itself. Under these conditions there is nothing to oppose the contraction of the surface — the tension is the same as that of pure water."

---

[1] *Phil. Mag.* **48**, 331 (1899).

[2] This curve is obtained from the data of Rayleigh as recalculated to absolute units by Freundlich, *Kapillarchemie*, p. 279 (1909).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

If the molecules "behave like smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely packed. According to this view the tension would remain constant up to the point where a double layer commences to form. It would then suddenly change, to remain constant at the new value until the second layer is complete. The actual course of the curve of tension deviates somewhat widely from the above description, but perhaps not more than could be explained by heterogeneity of the oil whereby some molecules would mount more easily than others, or by reference to the molecular motions which cannot be entirely ignores. If we accept this view as substantially true, we conclude that the first drop in tension corresponds to a complete layer one molecule thick, and that the diameter of a molecule of oil is about 1.0×10^{-7} cm."

Thus castor-oil only *begins* to have an appreciable effect on the surface tension of water when it is present in sufficient quantity to form a layer 1.3×10^{-7} cm thick. When however, the thickness of the film is increased beyond this point (S in Fig. 1), then the surface tension rapidly falls as is shown by the portion of the Curve ST. From this point on, the surface tension changes only slowly (Curve TV). Rayleigh attributes the slight decrease between T and TV to a "want of homogeneity" in the oil, that is, to the presence of impurities. He says: "It would seem as if the surface still retained an affinity for some minor ingredient capable of being extracted, though satiated as regards the principal ingredient."

With olive oil Rayleigh found the thickness at which the tension begins to fall is 1.0×10^{-7} cm.

Rayleigh thus believes that the point S (Fig. 1) corresponds to a layer one molecule deep and implies that the point T corresponds to a double layer of molecules.

Henri Devaux[1] has extended this work and has developed experimental methods for the study of oil films which are beautiful in their simplicity and remarkable in the clearness with which they demonstrate the existence of monomolecular oil films.

A photographic tray (Fig. 2) is half filled with water and a little clean powdered talc is dusted (through a piece of cloth) onto the surface. By blowing gently upon the surface, the talc, together with all accidental contamination, is blown to the further end of the tray. A strip of paper A, is then placed upon the surface of the water and held by the thumbs against opposite sides of the tray. By pushing along this barrier all the oil contamination is forced into the position C (Fig. 2), while the surface below A is a perfectly clean surface of water.

This clean surface is now lightly dusted with talc. A fine wire is dipped in the oil and any visible drop hanging to it is removed. The end of the wire is then touched to the center of the talc-covered water surface. Immediately the talc is pushed back from wire, forming a circular area of apparently clean water. If only a small amount of oil is applied this circle grows only to a limited

[1] Devaux has published a large number of papers between 1903 and 1914. A review of his work up to 1913 was published in the annual report of the Smithsonian Inst., 1913, p. 261. Subsequent papers are *Soc. franc. phys.* **55**, 3 (1914), and *Ibid.* **57**, 3 (1914).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

size. If oil is similarly applied to another part of the talced surface another circle will be formed without causing distortion of the first, unless the two circles come in contact. This proves that the surface tension of the oil covered water within the circles is the same as that of the clean talc covered surface.

Another experiment is still more instructive. Let us clean the surface as before and then sprinkle talc upon it. By blowing gently upon the water *all* the talc is readily pushed up against the barrier A. Now apply a very small amount of oil and then dust the oil contaminated surface with talc. By then blowing upon the water at the point D (Fig. 2) the talc moves back to the position E, but no further. The clear area about D is evidently clean water, while the talc-covered area F is covered by an oil film. The oil film thus covers a perfectly definite area without having any effect on the surface tension. To measure

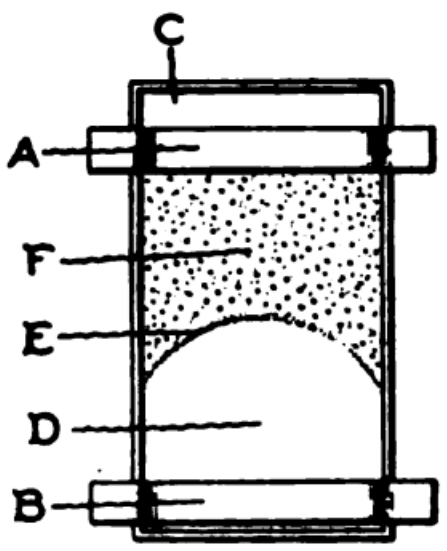


Fig. 2.

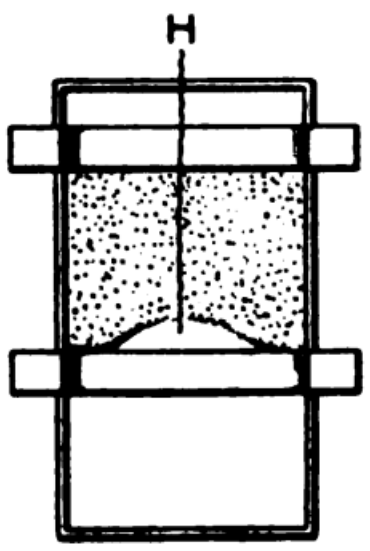


Fig. 3.

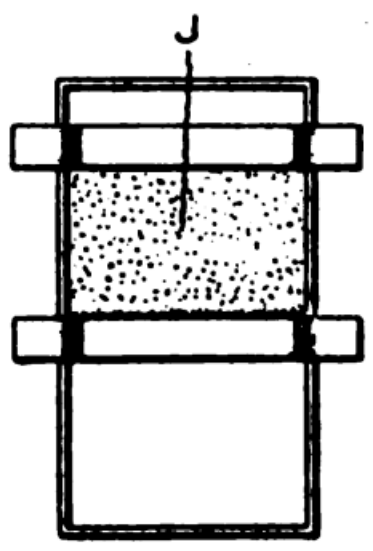


Fig. 4.

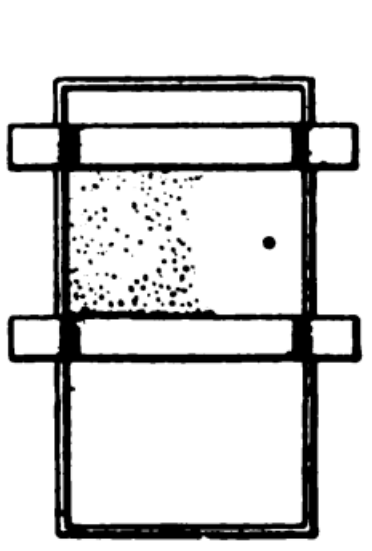


Fig. 5.

this area accurately it is only necessary to straighten the lower edge of the area F by means of the paper strip B. To accomplish this, blow continuously upon the surface (at D) while the strip B is advanced to the position shown in Fig. 3. Upon moving the barrier further the clear area H suddenly disappears as shown in Fig. 4. If the strip is moved still further the oil film behaves like an elastic stretched membrane and can be compressed or expanded at will. But if the lower barrier is pulled back below the position shown in Fig. 4 then the oil-covered surface ceases to expand and no longer follows the motion of the barrier.

This whole behavior is very similar to what we should expect if we had a tray with the bottom half covered by shot. By a movable partition all the shot can be pushed to one end or the other, but in any case they cover a definite area on the bottom of the tray. If we imagine the shot to be somewhat compressible and the tray to be subjected to vibrations of small amplitude (thermal agitation of molecules), so that some of the shot can more easily mount up on the others, then we seem to have a complete analogy to the phenomena described above.

Devaux has determined the areas covered by monomolecular films from weighed amounts of oils. To do this he prepares a dilute solution (1:1000) of the oil in pure benzene and places one or two drops of this solution upon

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the surface of the water. The benzene evaporates and leaves the oil. Knowing the volume of the oil added in this manner and the area covered by it, the thickness of the film is readily calculated. Devaux considers that this thickness represents the diameter of the molecule. In the case of triolein, he finds this thickness to be 1.1×10^{-7} cm. From Perrin's value for the Avogadro's constant and from the molecular weight and density of triolein, he calculates that the theoretical value for the diameter of a molecule of triolein should be 1.13×10^{-7} cm.

This result, considered together with whole behavior of the thin films, affords very conclusive proof that these films are really one molecule deep.

Devaux has studied films of solid substances by dissolving these in benzene. He finds that these also form monomolecular films and even in this condition, exhibit the properties of solids. That is, the films possess a transverse rigidity which disappears as soon as the amount of substance per unit area is less than that corresponding to the monomolecular film. From this fact Devaux derives "This general conclusion: the characteristic mechanical properties corresponding to certain states of a body, the surface tension of a liquid or the rigidity of a solid, persist almost intact down to molecular thicknesses, disappearing abruptly the minute we go further."

The work of Rayleigh and Devaux has not attracted the attention which it deserves. The above conclusion of Devaux's, so well supported, in some cases, at least, by experimental facts, is not at all in accord with the commonly accepted theories of surface tension, but it is exactly in line with the theories of adsorption, catalytic action, etc., which have been outlined in Part I of this paper.

Marcelin[1] describes some interesting experiments with films of oleic acid. A monomolecular film made visible by talc was produced in the manner indicated by Figs. 2, 3 and 4. Then a drop of oleic acid of considerable size was placed on one side of the oil-covered surface (Fig. 4). Immediately the drop of acid spread out, pushing back the talced surface, as indicated in Fig. 5, to about one-half its original area. Marcelin reasoned that the monomolecular film had been changed to one two molecules thick. He generalized this conclusion and claimed that with all oils, a layer one molecule thick had no effect on the surface tension of water, while a layer two molecules thick could remain in equilibrium with a large globule of oil. This conclusion was also in accord with the observations of Rayleigh.

Devaux, in replying to Marcelin's paper, claimed that the ratio between the two areas (Fig. 5) was never as great as 1:2. For oleic acid he found 1:1.8, and for other oils, values of about 1:1.3. He therefore concluded that these thicker films were not two molecules thick, but were monomolecular films with closer packing of the molecules.

---

[1] *Loc. cit.*

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Labrouste[1] obtained monomolecular films of palmitic and stearic acids, and of myristin, laurin, stearin, palmitin, benzion, cetyl alcohol, etc. Sulfur and triphenylmethane could not be made of form monomolecular layers.

Cause of the Spreading of Oils on Water

To make further progress in the study of oil films, it is important to know what is the cause of the spreading of the oil upon the water. The problem is very greatly simplified by the knowledge that the films formed are one molecule thick.

It is natural to assume that the force which causes the spreading is due to an attraction between the group molecules of the oil and those of the water. From the chemical viewpoint developed in Part I of this paper, we should not regard this attraction as emanating from the molecule as a whole, but rather from certain atoms in the molecule. This would follows directly from our conclusion that the range of forces between atoms or molecules is of the order of 0.6×10^{-8} cm. Furthermore, it is evident that any attraction of the water for oil molecules *as a whole* would manifest itself as a solubility of the oil in the water. If, on the other hand, we can assume that a *portion* of the oil molecule is attracted to the water, while the remainder is more attracted to other oil molecules than to the water, then we have a ready explanation of the spreading on the water.

Let us consider oleic acid as an example. There is no doubt but that the carboxyl group has a marked affinity for water. The solubility of the organic acids in water, as compared with the insolubility of the corresponding hydrocarbons, is a clear indication of this fact. This affinity is due to the strong secondary valence characteristic of oxygen compounds. On the other hand, hydrocarbons have a greater affinity for each other than for water, since they are usually miscible with each other in nearly all proportions, although they are insoluble in water.

Therefore, when oleic acid is placed on water, it is probable that the carboxyl groups *do actually dissolve* in water; that is, they combine with the water chemically (by secondary valence). The long hydrocarbon chains have too much attraction for each other, however, and too little for water, to be drawn into solution merely because of the affinity of the carboxyl for the water.

As a matter of fact, by the spreading of the oil on the surface as a monomolecular layer, the carboxyl group can combine with all the water it requires, without causing the hydrocarbon chains to separate from one another.

The spreading of an oil upon water is thus due to the presence of an "active group" in the molecule; that is, some group which has a marked affinity (secondary valence) for water. This leads directly to the prediction that on oil without active groups, such as pure paraffin oil, should not spread at all. Experiment

[1] *Compt. rend.* **158**, 627 (1914).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

shows that this is actually the case. Hardy[1] has studied the spreading of many oils upon water and found that pure saturated hydrocarbons do not spread; neither do such substances as benzene, cymene, etc. In attempting to explain this fact, Hardy says, "The great chemical stability of the paraffins makes chemical interaction with water impossible. Some degree of chemical action would seem to be necessary to make one fluid spread as a film between two others (air and water)." He does not, however, go further than this in explaining the mechanism of the spreading. Hardy believes that the oil films are usually many molecules thick.

According to our theory of the spreading of oil films, the group molecules of oleic acid arrange themselves upon the surface, so that each carboxyl group is in contact with and is combined with water, while the hydrocarbon tails are packed in side by side and vertically placed above the carboxyl layer. The upper surface of the oil film thus consists of CH_3 groups. It is therefore evident that there should be no particular tendency for another layer of oil molecule to spread out on top of the first to form a second layer. In fact, since this upper surface consists exclusively of CH_3 (or C_2H_5) groups, while in a globule of oleic acid, carboxyl groups are distributed through the mass, it is natural that the oil should prefer to remain as globules, rather than spread out as a layer two molecules deep. In the mass of liquid the carboxyl groups probably tend to gather into clusters, because of the greater affinity of these groups for each other than for the hydrocarbon chains. This tendency to form minute clusters explains many of the phenomena observed by Devaux in connection with his study of films thicker than monomolecular.

Now Marcelin claims that oil films in equilibrium with globules of oil consist of double layers of molecules — a result inconsistent with the above theory. The best example that Marcelin finds in support of his theory is oleic acid. The molecule of this substance contains, besides the hydrocarbon chain, two distinguishing factors: the carboxyl group and the double bond. The marked difference between the freezing points and other properties of oleic and stearic acids, suggests that the double bond may play an important role in the spreading of oils on water.

In general, from the data available, it seems that the presence of a double bond increases the solubility of a compound in water. Thus ethylene and propylene are several times more soluble in water than ethane and propane. Crotonyl alcohol, C_4H_9OH, is soluble in about 6 parts of water, while butyl alcohol, C_4H_9OH, requires 12. Hexanyl alcohol is given as "very soluble", while hexyl alcohol is "slightly soluble".

This suggests that the double bond as well as the carboxyl groups, may be drawn down onto the surface of the water, if there is only a limited amount of oil on a large surface of water. When a globule of oil is placed on a limited

[1] *Proc. Roy. Soc.* **86A**, 610 (1912).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

surface, however, the carboxyl groups displace the double bonds. Thus the film is one molecule deep, but in the first case the molecules are partly reclining on the surface, while in the second they are packed tightly side by side and are more or less erect upon the surface.

Fortunately, the experiments with oil films furnish means for testing this theory. Rayleigh, Devaux, and Marcelin determined the thickness of oil films and assumed this to be the same as the diameter of the molecule of oil. From the present theory we are led to believe that molecules of oil on water are oriented and packed in the surface layer so that they cannot, even approximately, be regarded as spherical. We can, however calculate the area covered by each molecule as easily as we can calculate the thickness of the film. This area is equivalent to the average cross-section of the molecule in a plane parallel to the surface of the water. The thickness of the film is equivalent to the length of the molecule in a direction perpendicular to the surface.

If the square root of this cross-section differs materially from the thickness of the film, we have direct evidence that the molecules are not spherical.

Determinations of the Shapes of Group Molecules

In order to determine the cross-sections and lengths of molecules in oil films, experiments similar to those of Marcelin were undertaken. The oil, or solid fat, was dissolved in freshly distilled benzene (usually 50 mg in 100 cc.), and, by means of a calibrated dropping pipet, one or two drops of the solutions were placed upon a clean water surface in photographic tray. The maximum area covered by the film was measured by the method indicated in Figs. 2, 3 and 4.

Dividing this area by the number of molecules of oil on the surface, the area of water covered by each molecule is readily obtained. This must also

TABLE I

Preliminary Measurements of Cross-Sections and Lengths of Molecules

Substance	Formula	I Cross-section sq. cm	II $\sqrt{\text{Cross. sec.}}$ cm	III Length cm	IV Length per carbon atom
Palmitic acid	$C_{15}H_{31}COOH$	21×10^{-16}	4.6×10^{-8}	24.0×10^{-8}	1.5×10^{-8}
Stearic acid	$C_{17}H_{35}COOH$	22×10^{-16}	4.7×10^{-8}	25.0×10^{-8}	1.39×10^{-8}
Cerotic acid	$C_{25}H_{51}COOH$	25×10^{-16}	5.0×10^{-8}	31.0×10^{-8}	1.20×10^{-8}
Tristearin	$(C_{18}H_{35}O_2)_3C_3H_5$	66×10^{-16}	8.1×10^{-8}	25.0×10^{-8}	1.32×10^{-8}
Oleic acid	$C_{17}H_{33}COOH$	46×10^{-16}	6.8×10^{-8}	11.2×10^{-8}	0.62×10^{-8}
Triolein	$(C_{18}H_{33}O_2)_3C_3H_5$	126×10^{-16}	11.2×10^{-8}	13.0×10^{-8}	0.69×10^{-8}
Trielaidin	$(C_{18}H_{33}O_2)_3C_3H_5$	120×10^{-16}	11.0×10^{-8}	13.6×10^{-8}	0.72×10^{-8}
Cetyl palmitate	$C_{15}H_{31}COOC_{16}H_{33}$	23×10^{-16}	4.8×10^{-8}	41.0×10^{-8}	2.56×10^{-8}
Myricyl alcohol	$C_{30}H_{61}OH$	27×10^{-16}	5.2×10^{-8}	41.0×10^{-8}	1.37×10^{-8}

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

equal the cross-section of the molecules. The results are given in the first column of Table 1. The number of molecules of oil on the surface was found by first calculating the number of gram-molecules of substance in the one or two drops of benzene solution added, and then multiplying this by N, the number of molecules per gram molecule, which, according to Millikan, is equal to 6.062×10^{23}.

An examination of these results shows that the cross-sections of the molecules vary over quite a wide range—from 21 to 126×10^{-16} sq. cm. The three saturated acids, palmitic, stearic, and cerotic, all occupy nearly the same areas ($21\text{–}25 \times 10^{-16}$ sq. cm), notwithstanding the fact that the number of carbon atoms in the molecules increase from 16 to 26. Each tristearin molecule covers a space of 66×10^{-16}, which is exactly three times that of a stearic acid molecule. Furthermore, the molecule of cetyl-palmitate takes up an area of 23×10^{-16} sq. cm, which is again about the same as that of stearic acid.

Thus we see that each $-C(=O)-O-$ group occupies an area of about 23×10^{-16} sq. cm, no matter whether it occurs in an acid or in an ester. This area is substantially independent of the length of the hydrocarbon chain to which the active group is attached.

These measurements afford striking proof of the theory outlined in the preceding pages, according to which the spreading of an oil on water is caused by the presence of certain active groups in the molecule.

We may also calculate the length of the molecules in a direction perpendicular to the surface. The volume of each molecule is found by dividing the "molecular volume" of the oil (M/ϱ) by the Avogadro constant N. By dividing this volume by the cross-section of each molecule, the length of the molecule in a direction perpendicular to the surface can be obtained. The results are given in the third column of Table I.

It is interesting to compare these lengths with the cross-sections As a rough approximation we may assume that the dimensions of the molecule in directions parallel to the surface can be found by taking the square root of cross-section. This is equivalent to assuming that each molecule in the surface film occupies a volume represented by a square prism with its axis vertical. The length of the square side, which we shall refer to as the average diameter, is given in the second column of Table I, while the height of the prism (or the length of the molecule) is given in the third column.

It is seen at once that the molecules are very much elongated. Thus the length of the palmitic acid molecule is about 5.2 times the average diameter. The results prove that the molecules arrange themselves on the surface with their long dimension vertical as is required by the theory.

The molecule of tristearin has the same length (perpendicular to the surface) as the stearic acid molecule, but three times the cross-section. Thus

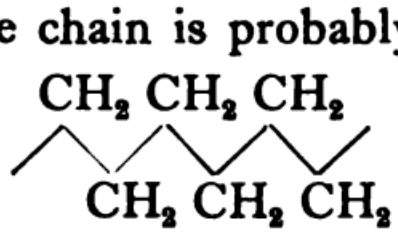
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

each of the three active groups has been drawn down on to the surface of the water while the hydrocarbon chains are packed in side by side and are erect upon the surface.

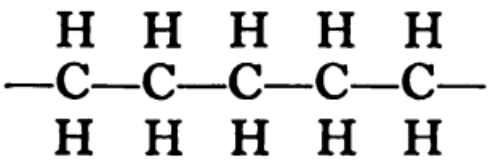
The case of cetyl palmitate is interesting Here the length of the molecule is 41×10^{-8} cm, or nearly twice that of the palmitic acid molecule, while the average diameter is only 4.8×10^{-8} cm, or about the same as the palmitic acid molecule. The molecule contains two long hydrocarbon chains connected by a carboxyl group. In palmitic acid the length of such a group is 24×10^{-8} cm. If the length of this group were nearly a constant quantity then we should have to assume that in the cetyl palmitate film the two chains in each molecule are arranged one above the other with the carboxyl in the middle. On this assumption, however, the only part of the molecule in contact with the water would be the CH_3 on the end of one of the hydrocarbon chains, so that there should be no tendency for this substance to form a monomolecular film on water. Solid paraffin for example dissolved in benzene and placed on water does not give a monomolecular film but gives a thick film (10–40 molecules thick), of variable thickness depending on the rate at which the benzene is allowed to evaporate.

The present theory therefore compels us to conclude that the carboxyl group of the cetyl palmitate is on the surface of the water and that both hydrocarbon chains are packed in side by side above the carboxyl group. The area of water covered by the carboxyl is the same as in the palmitic acid so that the two hydrocarbon chains side by side do not have any greater cross-section than the one in the palmitic acid. But each chain is extended to nearly twice the length in the first case that it is in the second.

This result indicates that the hydrocarbon chain does not have any definite shape or arrangement of its atoms in space, but rather that the chain should be regarded as extremely flexible. Thus in the palmitic acid film the arrangement of the atoms in the chain is probably somewhat as follows.



while in the cetyl palmitate the chains are packed more closely so that the arrangement becomes more nearly that represented by the typical formula:



In a diamond the distance between adjacent carbon atoms is 1.54×10^{-t} cm and this probably represents the minimum distance within which carbon atoms can approach. In the hydrocarbon molecule we should expect that they would be considerably further apart than this.

Dividing the length of the molecule (Table I) by the number of carbon atoms in the chain we obtain the average ***vertical distance*** between adjacent

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

carbon atoms in the chain. The results are given in the fourth column of Table I. In all cases except that of cetyl palmitate the distance is less than the distance between atoms in the diamond. This is a clear indication that the atoms cannot be arranged linearly but rather must be arranged along a zig-zag or curved line. The observed crosssection (23×10^{-16} sq. cm) is ample to allow the carbon atoms to be arranged in some such manner and still be separated from each other by distances greater than 1.54×10^{-8} cm.

The results obtained with the substances containing unsaturated hydrocarbon chains afford striking confirmation of the theory already proposed, according to which the double bond is to be regarded as an active group. Each oleic acid molecule covers a surface of 46×10^{-16} sq. cm whereas the saturated acids only cover about half as great a surface. This same difference is manifest in triolein and trielaidin when compared with tristearin. The data given in the fourth column shows this effect even more clearly. Whereas with all the saturated molecules the average vertical distance between carbon atoms is greater than 1.2×10^{-8}, it lies between 0.62 and 0.72×10^{-8} for the unsaturated molecules.

We thus have a proof that the film in equilibrium with a globule of oleic acid on water, which Rayleigh and Marcelin supposed to be two molecules thick, is in reality only one molecule thick. Marcelin found that the film in equilibrium with the glouble was about twice as thick as that obtained with the maximum extension. Since the latter is clearly one molecule thick Marcelin concluded that the former must be two molecules thick.

From the data of Table I, however, we see that an oleic acid film, in maximum extension, is only half as thick as that of stearic acid, so that, when doubled in thickness by placing a globule of oleic acid on the surface, the film becomes of the same thickness as that of stearic acid and the cross-sections of the molecules are also the same. There is thus no reason for assuming the existence of a layer two molecules deep.

These preliminary experiments furnish very convincing evidence of the correctness of the theory developed in the present paper.

To make further progress it became desirable to measure the forces involved in the spreading of oils, in other words to measure the changes in surface tension produced by oil or fat films. Rayleigh and Hardy had used Wilhelmy's method, but this method cannot be employed for measuring the forces exerted by solid films and even for liquid films great difficulty is caused by the glass or mica plates becoming greasy so that the angle of contact no longer remains zero.

In carrying out measurements of the areas covered by oil films by Devaux's method one is struck by the magnitude of the forces acting on the paper strips. If the strips are not very firmly attached to the edges of the tray, they may be pushed out of position when a drop of oleic acid is placed on the water. It occurred to the writer that a very satisfactory method of

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

measuring the forces could be developed by a horizontal balance arranged to weigh the force acting on one of these paper strips.

This new method not only avoids the difficulties in connection with contact angles and solid films, but has the marked advantage that it affords a highly sensitive and accurate *differential* method of measuring slight changes in the surface tension of water.

A diagrammatic representation of the apparatus used for this purpose is given in Fig. 6. The water is placed in an enamelled tray, T, which is

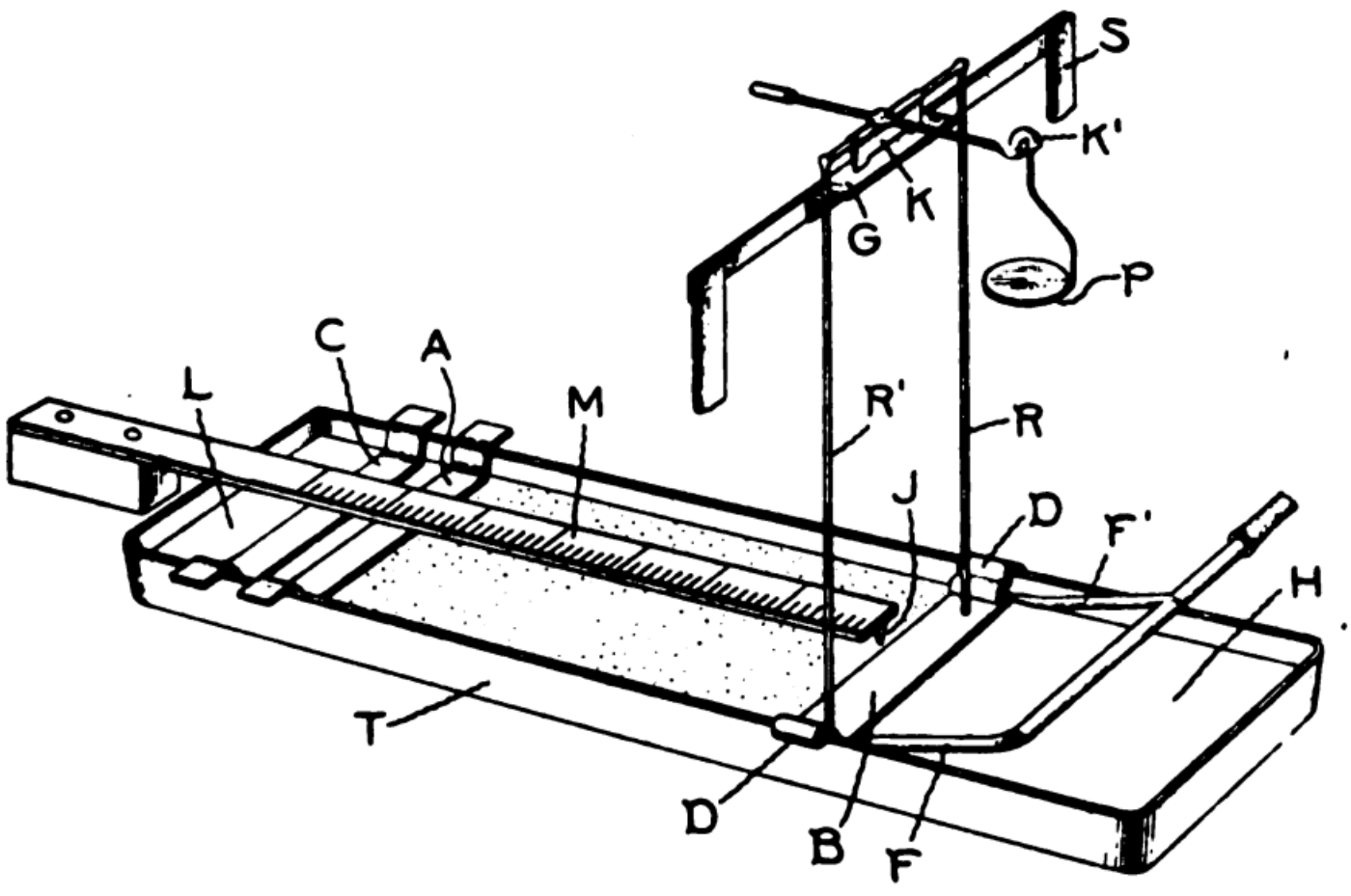


FIG. 6.

about 60 cm long and 15 cm wide. Above the tray is arranged a small balance with knife edge K resting on a glass plate, G, fastened to a support, S. One end of the beam of the balance has a counter-weight while the other has a small knife edge, K′, from which hangs a small pan, P. Two glass rods R and R′, cemented to the knife edge, extend downwards and pass through two small holes in a strip of paper, B, which floats upon the surface of the water in the tray. To prevent the paper from being softened by the water it may be prepared by dipping in a solution of paraffin in benzene.

The length of the paper strip B is about five mm less than the width of the tray, so that it can move freely without touching the sides of the tray.

The surface of the water between the strips A and B is covered by an oil film by placing one or two drops of a benzene solution of the oil on the water.

As the strip A is moved forward the oil film is pushed ahead of it until it begins to exert a force on the paper strip B. This force also tends to make the oil film flow around the ends of the strip B into the space H behind the strip. To prevent this, two air jets are directed by the tubes FF′ against the surface of the water between the ends of the strip B and

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the sides of the tray. The air blast is regulated and maintained constant by allowing a portion of the air to escape from a tube dipped to a given depth in water. Two pieces of sheet metal D and D′ are attached to the edges of the tray confining the air blast as much as possible to the surface of the water at the ends of the strip B.

Before beginning an experiment the air blast is started, impurities on the surface H are blown to the other side of B, and this surface of the water is cleaned by scraping with a strip of paper, C. All contaminating films are thus forced into the space L, from which they may be removed on to small pieces of paper dipped into the water. The air pressure or the balance is so adjusted that the center of the edge of the strip B is directly below the point J, which is fastened to the end of the meter stick M.

A weight of 50 mg is placed on the pan of the balance. This causes the rods R with the strip B to move (to the left in the diagram) until they strike a stop, which is not shown in the figure. The strip A is placed on the surface and is moved along until it is close to the strip B, to see if there is any residual contamination of the surface. Usually when A is brought within 5–10 mm of B the latter is caused to move along with A because of residual contamination. When the edge of the strip is under the point J, the force exerted by the oil film must be equal to the weight in the pan P, multiplied by the ratio of the lever arms of the balance (about 1:3). The distance between the strips A and B is then read off on the meter stick M, avoiding parallox by observing the reflection in the water surface. In this way the amount of residual contamination is determined. Owing to oil contained in dust in the air which settles on the surface, and to oil which adheres to the sides of the tray from previous experiments it is difficult to entirely avoid this contamination. However, by scraping the surface a few times after each experiment the amount of this contamination can be reduced to less than 1 cm with 50 mg on the pan, or one or two mm with 500 mg. This amount is practically negligible.

After thus making sure that the surfaces are clean one or two drops of the benzene solution are placed on the water between A and B and a 50 mg weight is placed on the pan. Strip A is then moved along until the oil film produces sufficient pressure against B to bring it under the equilibrium point J. A reading on the meter stick is taken. Then another 50 mg weight is applied and the strip A is again moved until equilibrium is reached. Weights of 50, 100 or 250 mg are thus added successively until the oil film has been compressed into a space of a few millimeters.

As a result of these measurements the force acting on the strip A may be plotted as a function of the area included between the strips A and B. A typical curve is that shown in Fig. 7.

The weights applied to the pan are plotted as ordinates while the distances in cm between A and B are plotted as abscissas.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

When the area is greater than a certain rather definite limit, Q, there is practically no force acting on the balance but as the area is decreased the force rapidly increases until it reaches a limiting value at the point H.

Both solid and liquid films were studied. With such a substance as palmitic acid, the surface of the water (as evidenced by dust particles) remains mobile only until the point S, Fig. 7, is reached. The whole surface then becomes rigid, that is, all dust particles on the surface become fixed in their relative positions. As the film is compressed beyond this point the whole surface moves as an elastic membrane. The film itself however, remains entirely invisible until a point beyond H is reached, when the solid surface begins to crumple and a peculiar appearance (strain lines) is often observed on the surface.

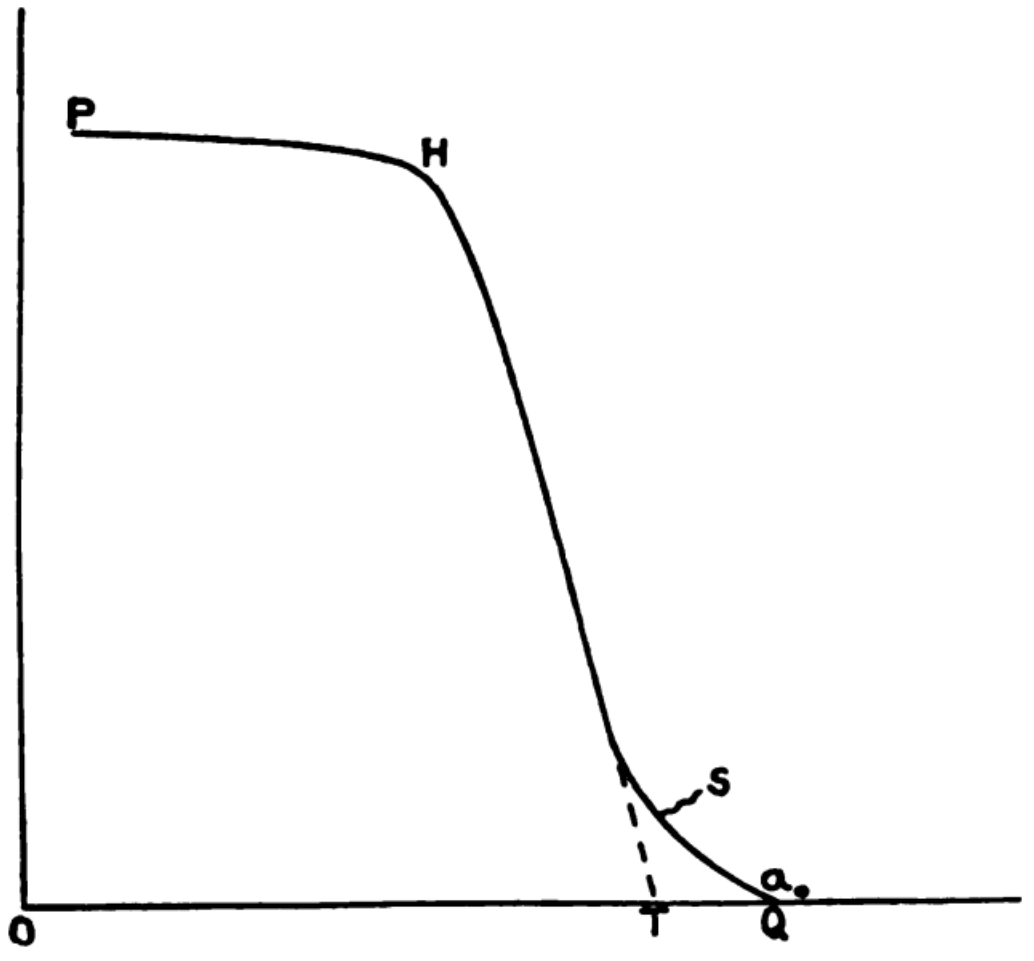


FIG. 7.

On the other hand, liquid films such as those produced by cetyl alcohol, or oleic acid, preserve their mobility even when compressed up to very small fractions of their original areas.

After a solid film has been crumpled up beyond the point H it will not expand again upon removing the pressure. The liquid films will spread out, but with marked hysteresis effects. To avoid these, all the measurements were made in regular sequence increasing the weights by regular increments. However, the curves obtained by adding 50 mg at a time were usually not materially different from those formed with 250 mg increments.

Experimental Results on the Forces Required to Compress Surface Films

A large number of fatty acids, alcohols, and esters have been studied by this method. Some of the results are given in Figs. 8 to 18. The curves are based on observations like those represented in Fig. 7, but the coordinates

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

are expressed in different units. The areas of water covered by the films were divided by the number of molecules of oil added, and the areas per molecule in sq. cm were thus calculated. These are plotted as abscissas while the forces acting on the films are expressed in dynes per cm and are plotted as ordinates. The unit used for the abscissas of the curves is 10^{-16} sq. cm per molecule.

In referring to these and similar curves in the following discussion we shall use a to denote areas per molecule and F to denote the force in dynes per cm with which the film resists compression. The coordinates of any particular point on the curve we shall indicate by subscripts, thus the coordinates of the point H in Fig. 7 are F_H and a_H. The letter H is used to denote a kink in the curve at which the slope (as a decreases) becomes *horizontal* or nearly so. The letter V denotes a kink where the slope suddenly increases so that the curve tends to become *vertical* (for example in Fig. 11). The value of a corresponding to the point O will be usually denoted by a_0, since the ordinate of this point is $F = O$.

The substances studied by this method included acids, alcohols and esters of saturated and unsaturated aliphatic hydrocarbons.

The materials used differed very considerably in purity. The samples of lauric, palmitic, stearic and oleic acids, and the ethyl palmitate were of high purity and were kindly given by Prof. W. D. Harkins. Arachidic, myristic, cerotic and erucic acids, cetyl and ceryl alcohol, ethyl palmitate, amyl strearate and cholesterol were furnished from the chemical museum of Columbia University through the kindness of Prof. J. L. R. Morgan. The amyl stearate, arachidic acid and ethyl palmitate appeared to be of high purity, but the erucic and myristic acids and cholesterol were of doubtful purity. Samples of myricyl alcohol, cerotic acid, cetyl alcohol and cetyl palmitate, and oleic acid, of a high degree of purity, were prepared in this alboratory by Mr. Harold Mottsmith. Samples of myricyl and cetyl alcohols, oleic, cerotic, myristic, arachidic and linoleic acids were purified by fractional distillation in very high vacuum (pressure lower than 0.0001 mm of mercury). Samples of linoleic and linoleic acids from a well-known manufacturer (in sealed tubes) were also available. The specimens of triolein, trielaidin, tristearin, and ricinoleic acid were prepared by Mr. Mottsmith without attempting to get very high purity. Samples of oils such as linseed, cottonseed, soya bean, etc., purified by his special process were kindly furnished by Dr. Charles Baskerville.

Saturated Acids.—Lauric ($C_{11}H_{23}COOH$), myristic ($C_{13}H_{27}COOH$), palmitic ($C_{15}H_{31}COOH$), stearic ($C_{17}H_{35}COOH$), arachidic ($C_{19}H_{39}COOH$) and cerotic ($C_{25}H_{51}COOH$) acids were investigated. Lauric acid proved too soluble in water for reliable measurements, the films contracting in area during the course of the measurements. Myristic acid showed some indications of solubility but not enough to interfere seriously with measurements. The curve obtained

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

with a film of pure palmitic acid on distilled water at 16° is given in Fig. 8. The point marked S is that at which the film became solid.

The value of a_0 is about 21.8×10^{-16}.

The force necessary to compress the film to $a_H = 13 \times 10^{-16}$ sq. cm is about $F_H = 63$ dynes per cm. This is nearly as great as the surface tension of pure water (73 dynes per cm).

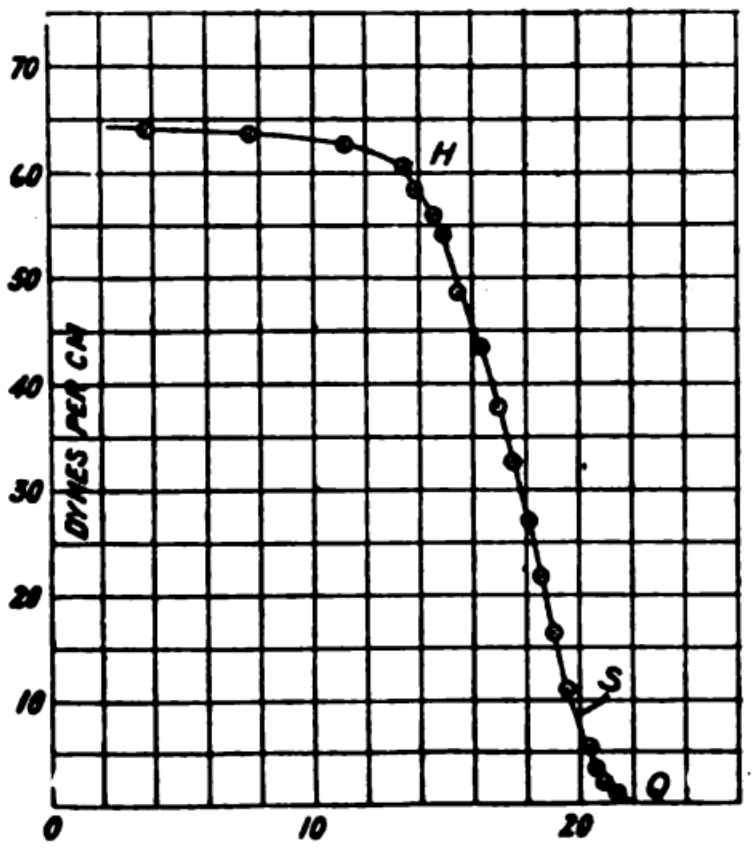


FIG. 8. Palmitic acid on water at 16°C.

The curves obtained with stearic, arachidic and cerotic acids on pure water at 16° were in all respects practically identical with those found for palmitic acid (Fig. 8).

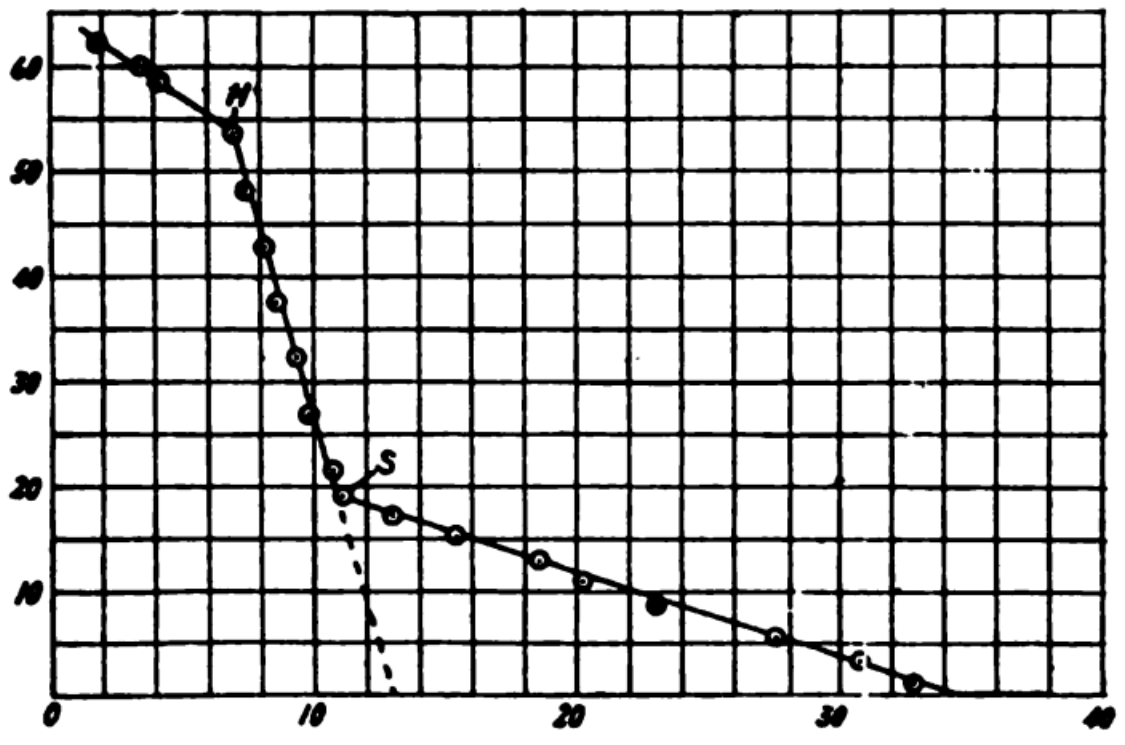


FIG. 9. Palmitic acid on water at 45°.

Upon cooling the water to 4° the curves still remained unchanged. With the water at 45° the curve for palmitic acid (but not the higher fatter acids) changed to the form given in Fig. 9. Up to the point marked S the film remained liquid. Evidently then, the melting point of the film is a function

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

of the area available per molecule. At this higher temperature the value of a_0 for palmitic acid is very materially greater than at lower temperatures, namely, 34×10^{-16} instead of 21.8×10^{-16} sq. cm.

Extremely interesting effects are observed when very small quantities of hydrochloric or sulfuric acids are added to the water. Figs. 10, 11 and 12 illustrate the curves obtained with water at 16° containing 0.1% of hydrochloric acid (0.028 *N*). The points marked S indicate where the films become solid. For comparison, the curve (Fig. 8) normally obtained in the absence of the mineral acid is shown as a dotted line in each figure. It is interesting to note that the first kinds in the curve (marked H in Figs. 10, 11 and 12) occur at points which lie approximately on the normal curve (dotted line).

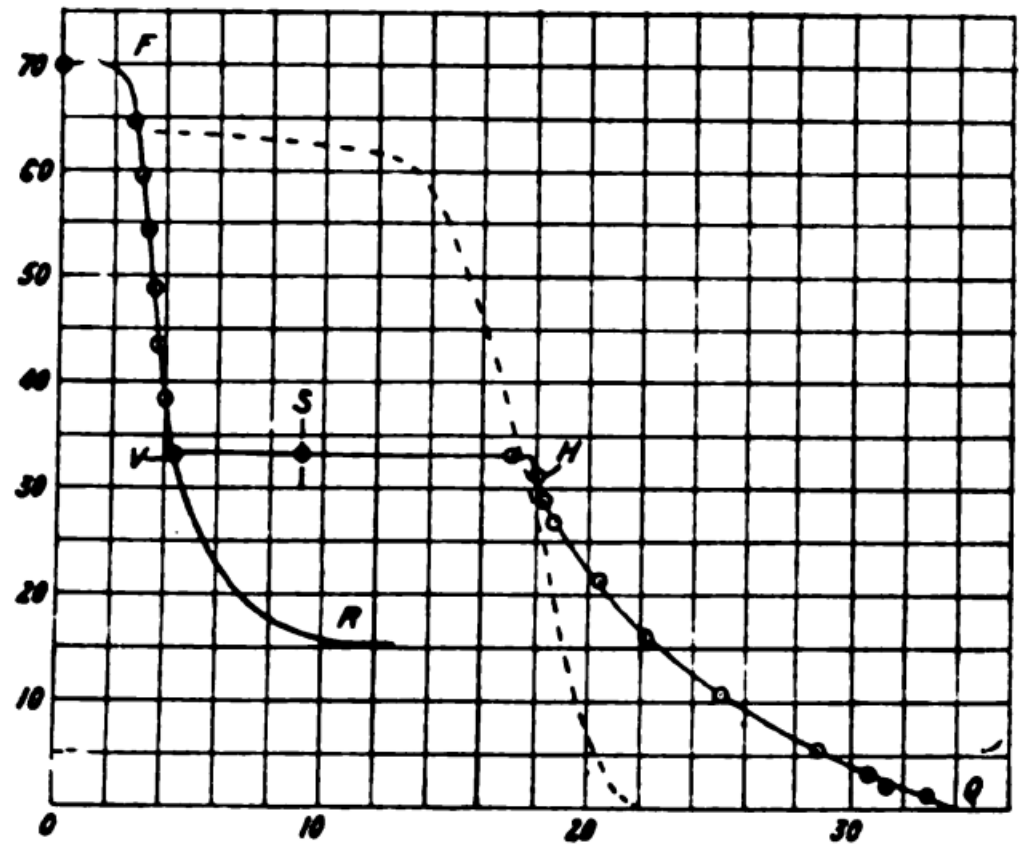


FIG. 10. Palmitic acid on water containing 0.1% HCl.

In carrying out these measurements the weights were placed on the pan of the balance and then the paper strip A (Fig. 6) was moved along until the movable strip B came to rest under the point J. When the point H on the curve was reached it was found that the strip B would not remain permanently under the point J but would very slowly move to the left. In order to keep the strip under the point it was necessary continually to advance the strip A. At first this shrinking of the film was slow (about 10% in 30 seconds), but as the area decreased the shrinking became more and more rapid. The last third of the line NV (Figs. 10 and 11) was passed over in a few seconds. These results suggest that the transformation which occurs in the film is of the nature of a change in phase and that the rate of change depends upon the number of nuclei of the new phase present at any time. These phenomena were further studied by taking weights off the pan after the film had begun to shrink, that is, after the point H (Fig. 10) had been passed. By then putting back the weights one by one it was possible to observe the curve RV which forms a lower extension of the curve VF.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The force per cm which must be applied to cause shrinking to begin (at H) is somewhat variable and depends to a considerable extent upon the rapidity with which the readings are taken. For palmitic acid the ordinates of the kink H have been found to vary between 26 and 34 dynes per cm, the smaller force corresponding to the slower taking of the readings.

Experiments were undertaken at several temperatures and with many different strengths of hydrochloric acid. With palmitic acid the curves obtained at 4° were the same as those at 16° except that the ordinate of the point H was somewhat greater, about 30–38 dynes per cm. With impure arachidic acid at 16° the kink H occurred at about 60 dynes per cm, while at 35° it was observed at 48 dynes per cm.

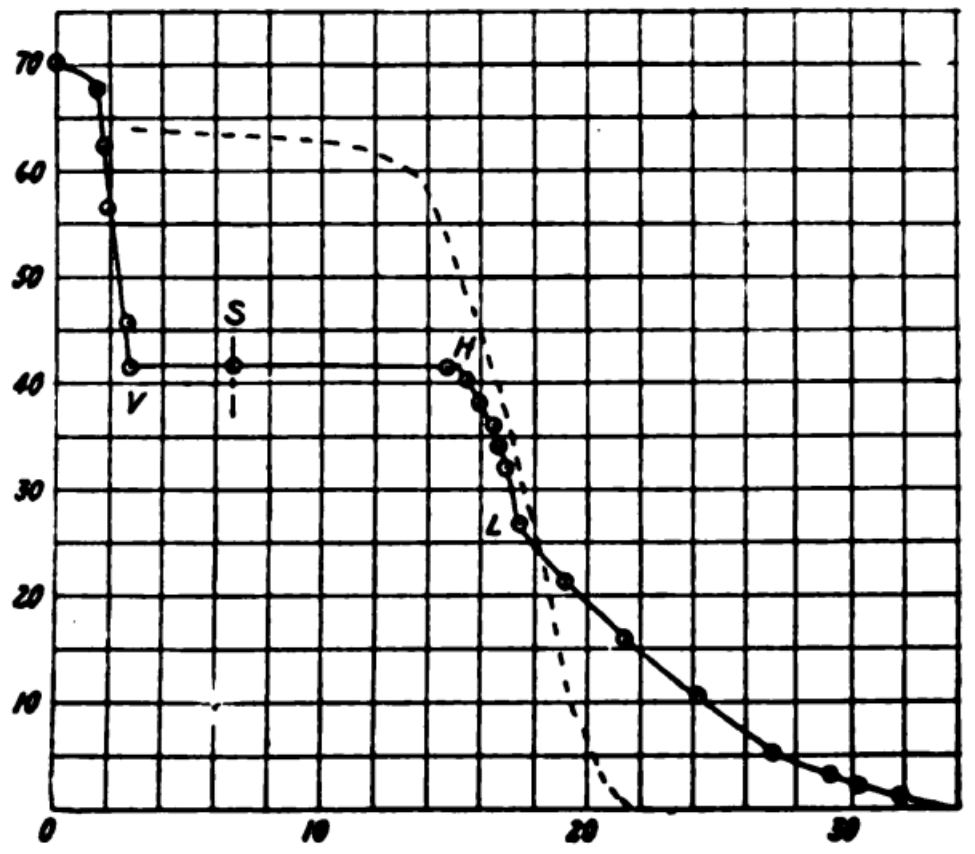


FIG. 11. Stearic acid on water containing 0.1% HCl.

Within wide limits the strength of the acid had no appreaciable effect on the curves. About one part of HCl in a million of water was sufficient to cause the curve to change from that shown in Fig. 8 to that in Fig. 10, and a 10,000 fold further increase in the strength made no further change. These films are thus extraordinarily sensitive to very small quantities of acid.

It was found that sulfuric acid gave exactly the same effect as hydrochloric acid. A small amount of hydrogen sulfide dissolved in the water gave a kink H as in Fig. 10, but the Curve VF was shifted much further to the right and the point Q came further to the left. The abscissa of H was about the same as for hydrochloric acid. In another case 0.2% of potassium cyanide, together with 0.01% of hydrochloric acid were added to the water. This gave a curve in which the kink H occurred at $a = 18.6 \times 10^{-16}$ sq. cm, $F = 27$ dynes per cm while the kink V occurred at $a = 11 \times 10^{-16}$ sq cm. The point Q was at $a = 26 \times 10^{-16}$.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

These results seem to show that as the hydrogen-ion concentration is made extremely small the Curve RF shifts to the right and the point Q shifts to the left, while the kink H remains practically fixed.

Curve I (Fig. 12) was obtained with a sample of arachidic acid of doubtful purity. The film became solid just before the vertical part of the curve (below H) was reached. The sample of the acid was then fractionally distilled in high vacuum, the first and last thirds being rejected. Curve II was then obtained. In this case the film became solid at the point marked S′ which is located in a position corresponding to those observed with palmitic and stearic acids (Figs. 10 and 11).

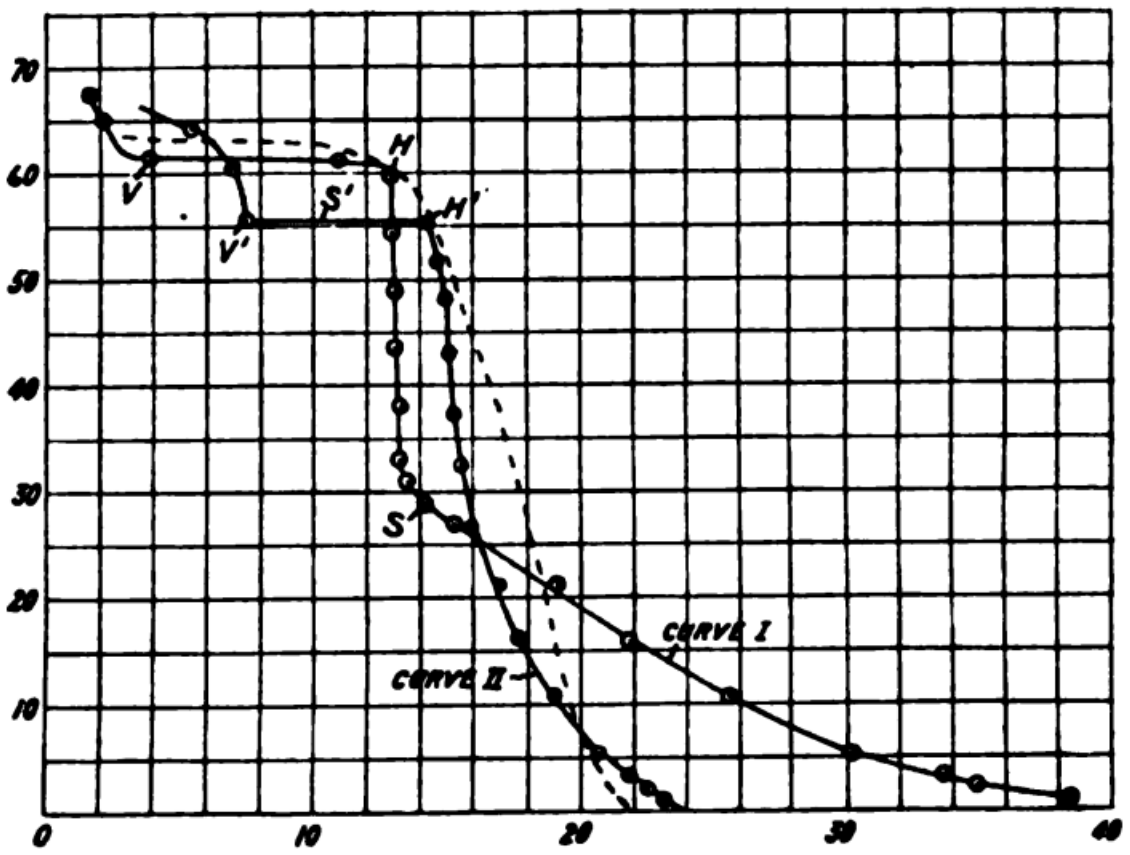


FIG. 12. Arachidic acid on water containing 0.1% HCl.

Myristic acid on 0.1% hydrochloric acid at 16° gave a curve very much like that found with palmitic acid (Fig. 10). The maximum area per molecule was, however, considerably greater, $a = 52 \times 10^{-16}$ sq. cm. The film became solid at a point corresponding to S in Fig. 10.

Cerotic acid films were not changed by the presence of hydrochloric acid, that is, the curves always resembled those of palmitic acid on pure water (Fig. 8).

With dilute solutions of salts such as the chlorides of sodium, calcium or magnesium the curves obtained are not very greatly different from those found with distilled water (Fig. 8). The small effects which do occur with these and other salts are being made the subject of further study.

Saturated Alcohols.—Cetyl ($C_{16}H_{33}OH$), ceryl ($C_{26}H_{53}OH$) and myricyl ($C_{30}H_{61}OH$) alcohols were studied. The curve obtained for cetyl alcohol is given in Fig. 13. The maximum area per molecule a_0, is 21×10^{-16} sq. cm which is about the same as that of the saturated acids on distilled water. The film of this substance is liquid even when compressed into a small area and even when the water is cooled to 4°. It would seem, therefore, that

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the compression and expansion of such a film should be practically reversible instead of showing the marked hysteresis observed with the solid films of the saturated fatty acids. This, however, is by no means the case. In compressing the film, the force must be increased as shown by the Curve QHU (Fig. 13). If now the weights are removed gradually no perceptible expansion of the film occurs until the point V is reached and then the area increases as shown by the curve VR. This hysteresis loop is not greatly different from those observed with solid films yet the cetyl alcohol film is extremely mobile.

Ceryl alcohol and myricyl alcohol give solid films. The curves obtained are, however, very similar to those of cetyl alcohol except that a_0 is considerably larger. With myricyl alcohol it seems to be difficult to get consistent results, perhaps owing to the great thickness and hence stiffness or rigidity of the

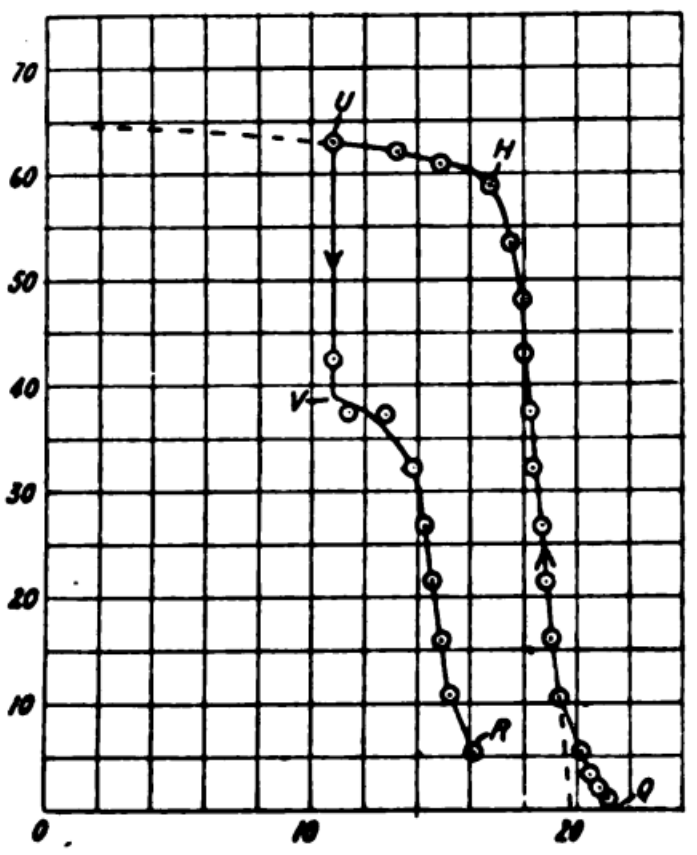


FIG. 13. Cetyl alcohol on water.

film. When one or two drops of the benzene solution is applied and the benzene has evaporated, it is found by sprinkling talc on the surface that the film has gathered into large cakes. When the area is decreased these cakes pack together leaving irregular spaces between them. On still further decreasing the area the cakes crush each other at their points of contact. It is therefore not surprising that the values of a_0 vary from about 20 to 31×10^{-16} sq. cm.

Within the range from 4 to 45°, temperature seems to have no important effect on the shapes of the curves obtained with these alcohols. The addition of hydrochloric acid to the water is also without apparent effect.

Saturated Esters.—Tristearine $(C_{17}H_{35}COO)_3C_3H_5$, cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$, amyl stearate, $C_{17}H_{35}COOC_5H_{11}$, and ethyl palmitate, $C_{15}H_{31}COOC_2H_5$, were the esters investigated. The curve for tristearine was of the same type as that of palmitic acid (Fig. 8). The value of a_0 was 68×10^{-16} sq. cm while the kink H occurred at $a_H = 48 \times 10^{-16}$ and $F_H = 61$ dynes per cm.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

With cetyl palmitate (Fig. 14) the curves obtained at different temperatures differed greatly. At 4° and at 16° the curves closely resembled those for palmitic acid (Fig. 8) and gave values of a_0 ranging from 20.5 to 25×10^{-16} sq. cm, while a_T (see Fig. 7) was always very close to 20.5×10^{-16}. At higher temperatures,

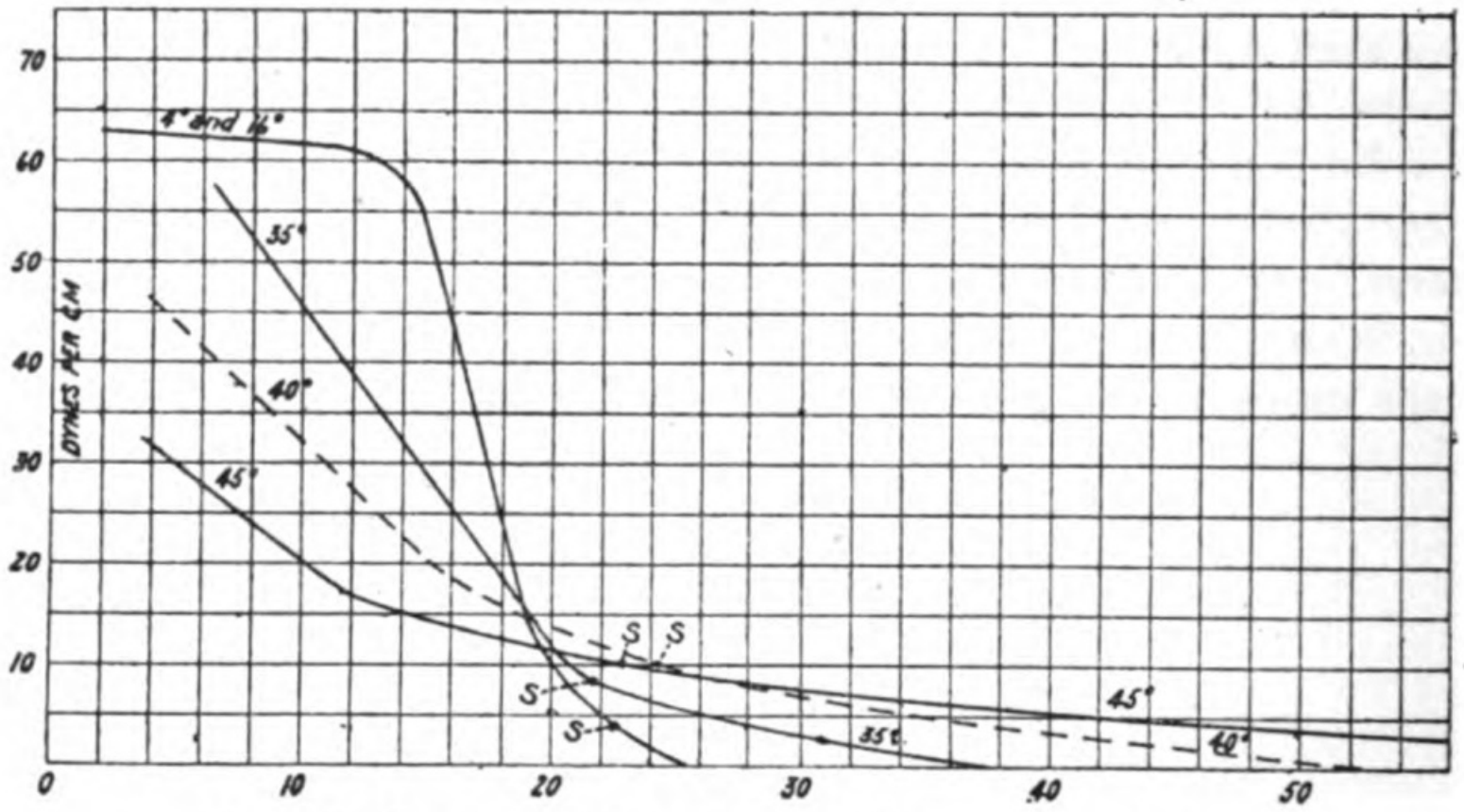


FIG. 14. Cetyl palmitate on water at different temperatures.

however, the value of a_0 increased to 37×10^{-16} at 35°, 52×10^{-16} at 40° and about 95×10^{-16} at 45°. At all temperatures the film became solid at approximately the same area of 23×10^{-16} sq. cm.

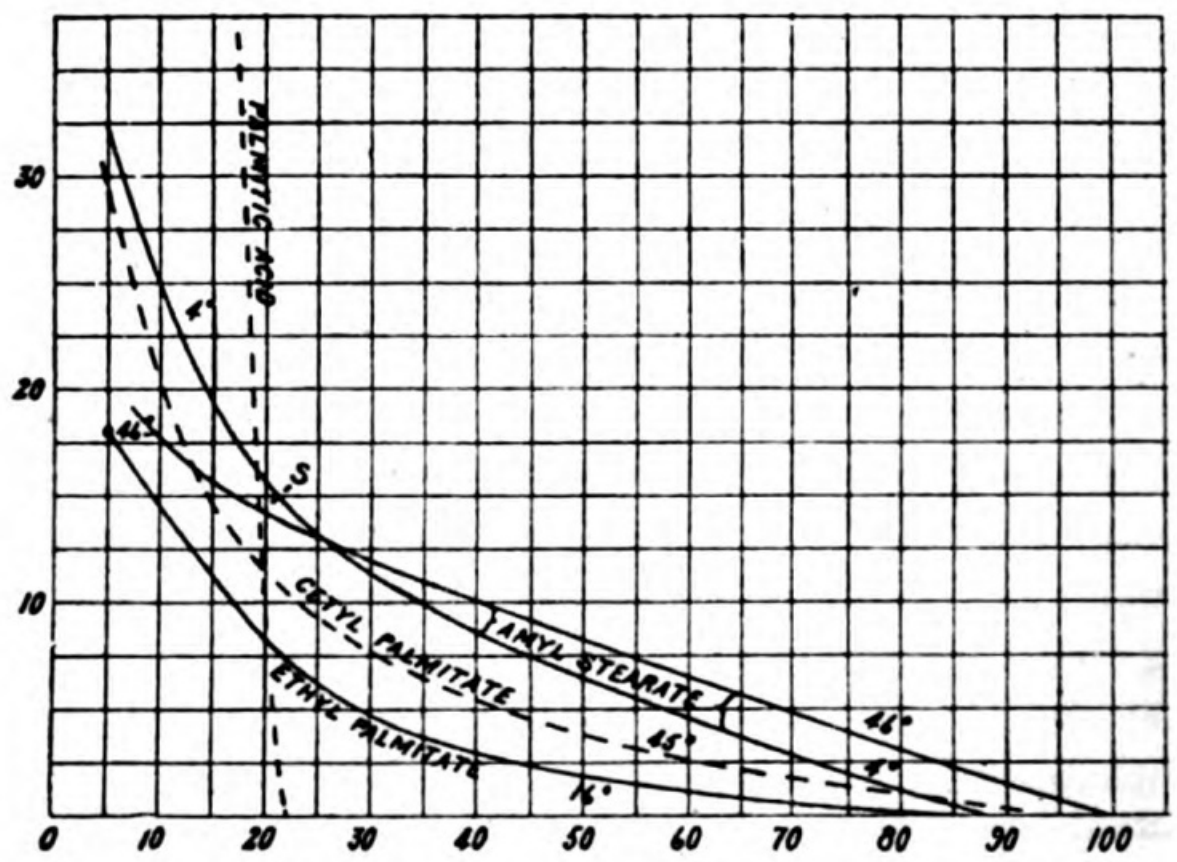


FIG. 15. Saturated esters on water.

Typical results with amyl stearate are shown in Fig. 15. At 4° the film became solid at the point marked S but at 16° and higher temperatures the film remained liquid even when greatly compressed. Between 4° and 46°, temperature had relatively little effect on the results except where the film became solid at 4°.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The area per molecule a_0 averaged about 95×10^{-16} sq. cm. The curves for amyl stearate thus resemble those obtained with cetyl palmitate at the highest temperatures. One dotted curve in Fig. 15 shows the results for cetyl palmitate at 45° as taken from Fig. 14 but replotted to the same scale as that used for the amyl stearate. A second dotted curve gives for comparison the data for palmitic acid as taken from Fig. 8.

Ethyl palmitate gives a rather similar curve which is also shown in Fig. 15.

Curves obtained with cetyl palmitate and amyl stearate on water containing hydrochloric acid did not differ materially from those on pure water.

Tristearin on 0.1% hydrochloric acid, on the other hand, gave a curve rather similar to that of stearic acid in Fig. 11. The value of a_0 was 108×10^{-16} sq. cm as compared to 68×10^{-16} for tristearin on pure water. The kink H occurred at a_H 53×10^{-16}; $F_H = 48$. The film of tristearin on the acidulated water remained liquid until the area per molecule had been reduced to $a = 21 \times 10^{-16}$ sq. cm.

Unsaturated Acids.—Oleic, $C_{17}H_{33}COOH$, erucic, $C_{21}H_{41}COOH$, linoleic, $C_{17}H_{31}COOH$, linolenic, $C_{17}H_{29}COOH$, and ricinoleic, $C_{17}H_{32}(OH)COOH$, acids were tried. The curves for oleic, linoleic and linolenic acids are given in Fig. 16. The data for palmitic acid (Fig. 8) is also given (as dotted curve)

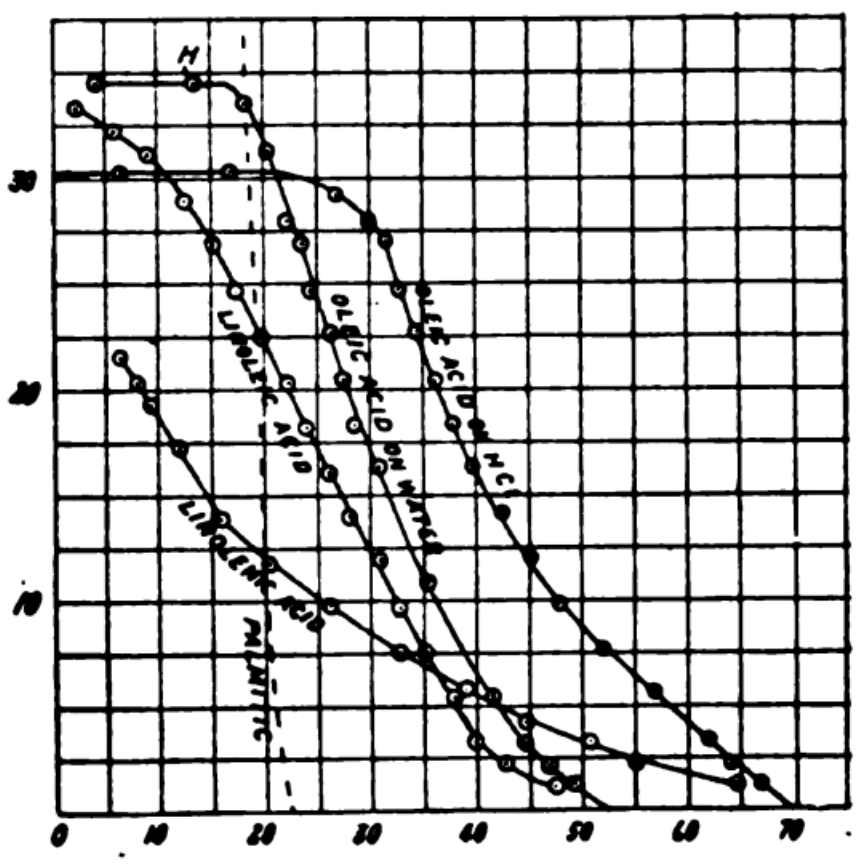


FIG. 16. Unsaturated acids on water.

for comparison. Hydrochloric acid in the water produces a marked effect on the oleic acid film causing it to increase in area as shown in the curve.

Erucic acid gave a curve very much like that of oleic acid (Fig. 16). The coordinates of the important points were

$$a_0 = 44 \times 10^{-16} \text{ sq. cm}$$
$$a_H = 12.6 \times 10^{-16} \qquad F_H = 36 \text{ dynes per cm}$$

The film remained liquid until very highly compressed.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Upon adding hydrochloric acid, the curve underwent approximately the same changes that occurred with palmitic acid, giving a curve similar to Fig. 10. The coordinates were

$a_0 = 82\times10^{-16}$ sq. cm
$a_H = 27\times10^{-16}$ $F_H = 26$ dynes per cm
$a_V = 7\times10^{-16}$ $a_S = 10\times10^{-16}$ sq. cm

Ricinoleic acid (Fig. 17) gave remarkable results. On distilled water no constant readings could be obtained until a force of more than 4 dynes per cm had been applied. With smaller forces the area would continually shrink, so that the curve obtained depended entirely on the rapidity with which the readings were taken. This part of the curve is indicated by a dotted line. On hydrochloric acids, as well as on various salt solutions, this tendency to shrink disappeared. The curve obtained with dilute hydrochloric (0.1%) is given in Fig. 17.

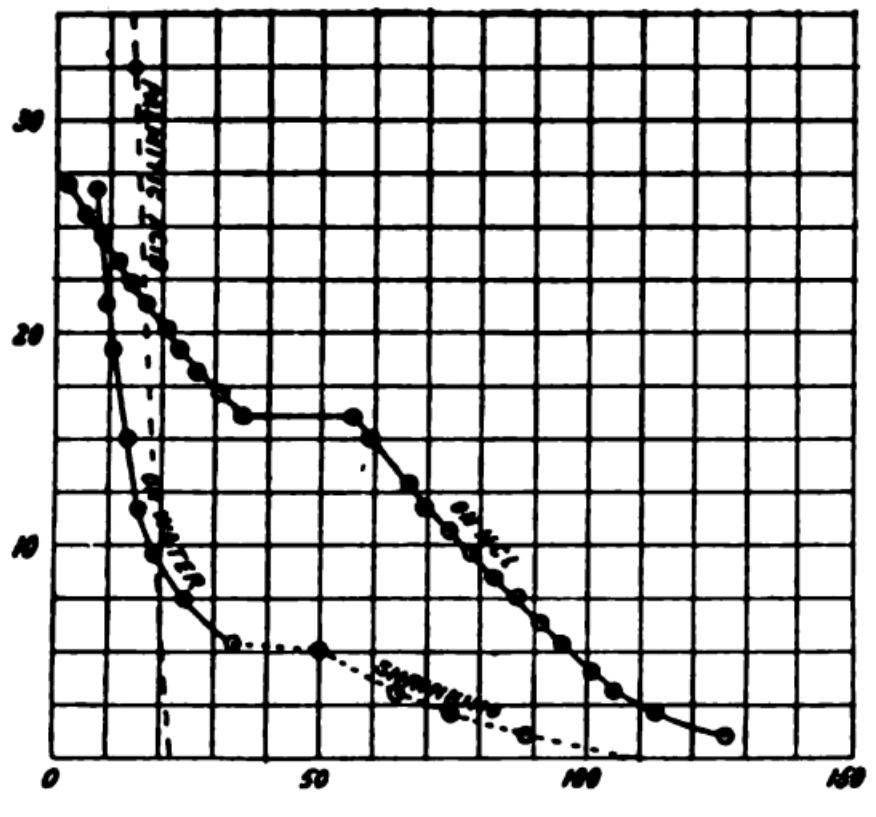


FIG. 17. Ricinoleic acid on water and on water containing 0.1% HCl.

Two kinks with a horizontal part of the curve between them were observed as in the case of the saturated fatty acids (Figs. 9 and 10). These results may be complicated by the presence of impurities.

Unsaturated Alcohols.—Anhydrous cholesterol was the only substance of this class investigated. The curve obtained resembled that with oleic acid on pure water (Fig. 16). The following values of the coordinates for the singular point were found:

$a_0 = 44\times10^{-16}$ sq. cm $a_S = 15\times10^{-16}$ sq. cm
$a_H = 11\times10^{-16}$ sq. cm $F_H = 45$ dynes per cm

The addition of hydrochloric acid to the water (0.1%) caused the curve to take the general character of the curve for palmitic acid on the acid (Fig. 10).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The constants were

$$a_0 = 72\times10^{-16} \text{ sq. cm}$$
$$a_H = 23 \text{ to } 28\times10^{-16}$$
$$F_H = 27 \text{ to } 35 \text{ dynes per cm}$$
$$a_S = \text{about } 10\times10^{-16} \text{ sq. cm}$$
$$a_V = 9\times10^{-16}$$

Unsaturated Esters.—Triolein $(C_{17}H_{33}COO)_3C_3H_5$, trielaidin $(C_{17}H_{33}COO)_3C_3H_5$, ethyl oleate, $C_{17}H_{33}COOC_2H_5$, linseed oil $(C_{17}H_{31}COO)_3C_3H_5$, castor oil $(C_{17}H_{32}(OH)COO)_3C_3H_5$, and many other oils were studied. Some of the results are given in Fig. 18.

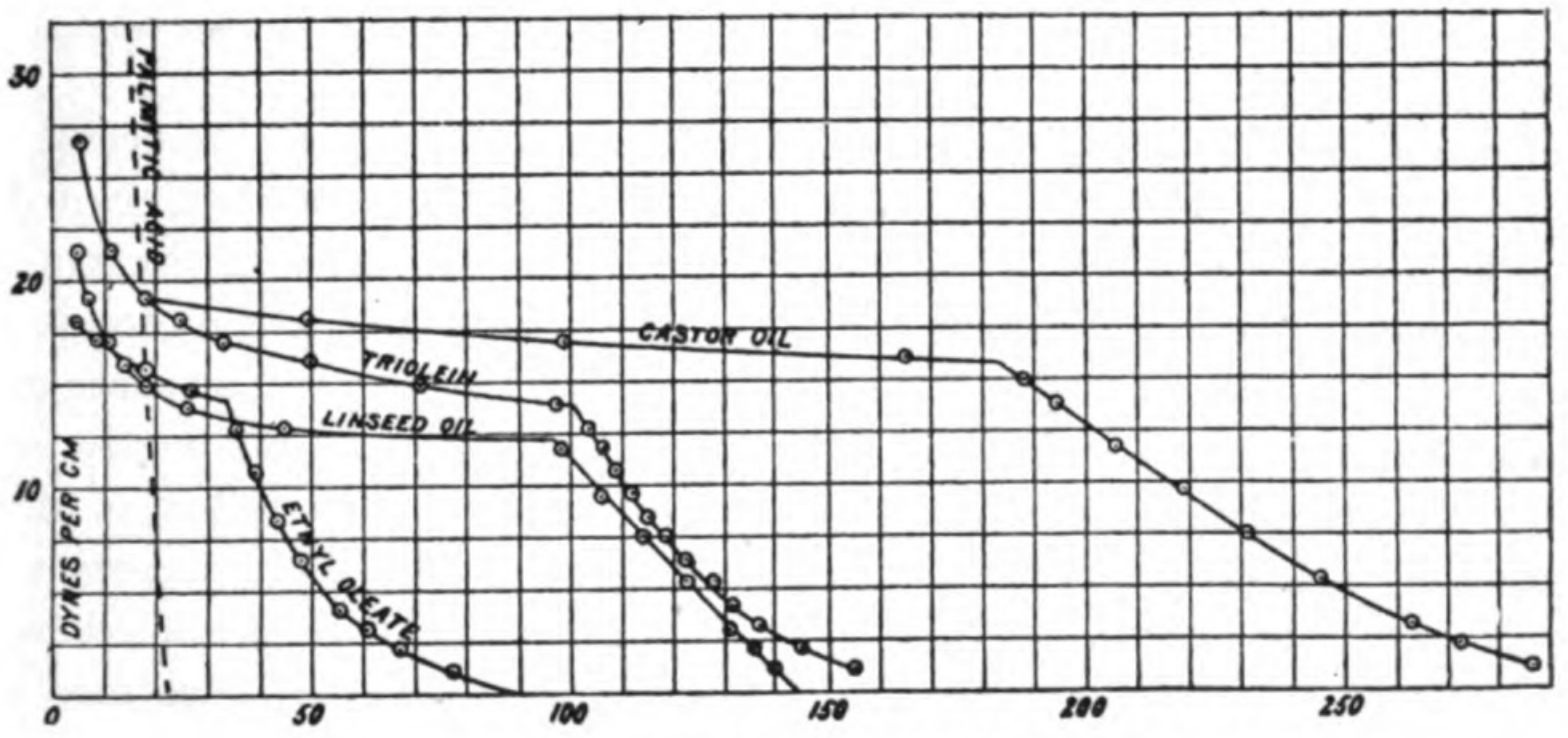


FIG. 18. Unsaturated esters.

The rising parts of the curve for small values of a may well be due to small amounts of saturated fatty acids or esters. The curve for trielaidin was practically identical with that of triolein.

Discussion of Results

These experimental results afford the strongest kind of confirmation of the theory that the spreading of films on surfaces is determined by the shapes of molecules and the relative activities of the different portions of the molecules. The maximum areas given in Table I are in substantial agreement with the values of a_0 taken from the curves in Figs. 8 to 18. The sharpness with which the force increases as the area available for the film is decreased is an excellent proof of the small range of the forces acting between the group molecules.

The saturated fatty acids (from palmitic to cerotic) cover approximately equal areas per molecule ($a_0 = 21\times10^{-16}$ sq. cm), irrespective of the length of the hydrocarbon chain. The glycerides cover about the same area as the fatty acids obtainable from them. The results with cetyl palmitate, amyl stearate, and ethyl palmitate show that the relations are not always as simple as this

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

and that the areas, even in the case of saturated hydrocarbon derivatives, are not always determined solely by the number of —COO— or other active groups present.

In the case of esters, such as amyl stearate, in which the molecules have two hydrocarbon chains of very unequal length, it is probable that a part, at least, of the hydrocarbon chain lies in the surface in contact with the water. We shall see, in another part of this paper, that with very dilute solutions of the lower members of the fatty acid series, the molecules lie spread out flat on the surface. Evidently this tendency exists to some extent among certain esters of the higher fatty acids, especially at high temperatures. We will postpone the further discussion of this subject until we have considered the results obtained in connection with the adsorption of fatty acids in the surface of their solutions in water.

The unsaturated fatty acids all cover much greater areas per molecule than the saturated. The double bond in oleic acid is thus apparently drawn down onto the water surface. It is interesting to note, however, that linoleic acid, with its two double bonds, does not cover any greater area per molecule than oleic acid. It may be that the double bonds attract one another to some extent in place of the water. Linolenic acid, however, with three double bonds, covers a considerably greater area than oleic or linoleic. As the number of double bonds increases, the energy consumed in compressing the film decreases (see Fig. 16), probably because the —COO— groups tend to be attracted by the double bonds in adjacent molecules and are thus more easily separated from the water surface.

The molecule of ricinoleic acid appears to lie almost wholly flat on the surface, the value of a_0 being in the neighborhood of 110×10^{-16} sq. cm. In this molecule there are three active groups: carboxyl, hydroxyl, and the double bond. These three together should not cover more than $60\text{–}70 \times 10^{-16}$ sq. cm. The value $a_0 = 110 \times 10^{-16}$, corresponds to a film thickness $\tau = 4.7 \times 10^{-8}$ cm, which is about what we should expect for a hydrocarbon molecule spread out flat on the surface. The castor oil (triricinolein) molecule is also evidently spread out flat on the surface.

The presence of the sharp kinks in the curves, such as H and V, makes it evident that several different processes are often involved in the compression of a film, and that these occur one at a time. Thus, in compressing a palmitic acid film (Fig. 8) between Q and H the molecules are being squeezed together more and more tightly, but without involving any radical change in their relative positions. When the point H is reached, the film begins to crumple up, probably by the folding of the whole film, but possibly by tearing molecules one by one from the surface of the water and squeezing them into a second layer on top of the first.

The kink S in Fig. 9 and in Curve I, of Fig. 12, are undoubtedly due to the solidification of the film.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

With films which are liquid, as, for example, cetyl alcohol films, the kink H probably occurs when the active group is forced away from the water surface and a second layer of molecules begins to form.

In attempting to account for the remarkable curves obtained with films of fatty acids on acidulated water, it is important to bear in mind that the curves (Fig. 8) obtained on pure water represent wholly irreversible conditions. Even with a liquid film (Fig. 13), the Curve UVR obtained by expanding the film, does not even approximate that obtained during compression (QHU). This is probably to be explained as follows: At the point Q all the molecules of cetyl alcohol lie on the surface with the OH group in contact with the water and the hydrocarbon chains vertical. As the force of compression is increased, the molecules are subjected to forces quite analogous to those acting on a watermelon seed squezezed between the fingers. In this latter case a very considerable pressure may be exerted before the seed moves at all; when it does, however, it is projected with high velocity. Similarly, the molecule of cetyl alcohol may be acted on by strong forces without causing it to be pulled away from the water surface. When the force reaches a certain value, however, the molecule is ejected. The energy involved may be much greater than that theoretically required to separate an OH group from the water surface. This ejection of molecules first begins when the point H is reached.

Now after a molecule has been forced into the second layer, its active group cannot come in contact with the water at all. If the force on the film is decreased (as at U in Fig. 13), the film therefore does not at first tend to spread. If the force is sufficiently decreased (for instance, to V), then the thermal agitation causes some gaps in the first layer to form from time to time, and into these the molecules in the second layer may descend until they come in contact with the water. This causes a spreading of the film.

The presence of hydrochloric acid in the water seems to cause an increase in the effective volume of the —COOH group, probably by adsorption of hydrogen ions. When the film is compressed the hydrocarbon chains are thus held so far apart at their lower ends that they cannot pack together in the manner necessary to form a solid film. As the force is increased, the adsorbed ions (?) on the —COOH groups are forced off until (at L, Fig. 11) the —COOH groups occupy the same area as if no acid were present. The film, for some unknown reason, remains liquid (except Curve I, Fig. 12), and the molecules are thus more easily ejected (at H) into the second layer. The hydrogen ions thus act as a catalyzer in two ways: by increasing the mobility of the film and by making it easier for the molecules to pass into the second layer. This is not caused, however, by any decreased attraction between the water and the —COOH group[1].

[1] This conclusion is based on the fact, discussed in a forthcoming paper by Harkins, that the surface tension at the interface of oils is not appreciably affected by the presence of acid.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The action of hydrochloric acid on these films is undoubtedly intimately related to the action of acids in catalyzing esterification. It must also be connected with the potential changes observed by Haber and Klemenciewicz[1] and others.

The Structure of Adsorbed Films on the Surface of Liquids[2]

The films of oil or solid fats described in the preceding section differ from other adsorbed films only by their insolubility and non-volatility. When a soluble fatty acid or alcohol is dissolved in water, or when the vapor of a substance like hexane or benzene is brought into contact with water, the surface tension is very materially decreased. According to the principle enunciated by Gibbs, this indicates that the dissolved substance or the vapor is adsorbed in the surface.

From the viewpoint developed in this paper we should expect that these adsorbed films in general should consist of not more than a single layer of molecules.

By means of Gibbs' equation[3],

$$q = -\frac{c}{\mathrm{RT}}\frac{d\gamma}{dc}, \tag{1}$$

the amount of material q adsorbed per sq. cm of surface may be calculated from the rate at which the surface tension γ varies as the concentration of the dissolved substance changes. The equation may also be applied to the depression of surface tension caused by a gas or vapor above the liquid.

It was pointed out by Milner that when substances which strongly depress the surface tension are added to water, the surface tension is a linear function of the logarithm of the concentration of the dissolved substance for all except very dilute solutions. We may write Equation 1, as follows:

$$q = -\frac{\mathrm{I}}{\mathrm{RT}}\frac{d\gamma}{d\ln c} \tag{2}$$

If γ is a linear function of ln c then q will be independent of the concentration. Milner thus calculates from Whatmough's data for acetic acid solutions that q is 3.8×10^{-10} mols per sq. cm over a rather wide range of concentration. The constancy of q under these conditions is readily explained according to our theory as being determined by the number of molecules needed to form a single layer. If we multiply Milner's result for q by N we find that the amount

---

[1] *Z. physik. Chem.* **67**, 385 (1909).

[2] A brief preliminary account of part of the work described in this section has appeared in the *Proc. Nat. Acad. Sci.* **3**, 25 (1917).

[3] A simple derivation of this equation is given by Milner (*Phil. Mag.* **13**, 96 (1907)). In this derivation it is not assumed that the gas law $pv = \mathrm{RT}$ holds in the surface layer; it is only necessary that it should hold for the osmotic pressure inside the solution, or in the case of adsorbed vapors, for the vapor above the liquid. The equation thus rests on a firm foundation, at least in the case of dilute solutions.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

adsorbed corresponds to 23×10^{13} molecules per sq. cm. The area occupied by each molecule is thus 43×10^{-16} sq. cm. This result is in fair agreement with the value 22×10^{-16} which we have found for films of the higher fatty acids on water. It is probable that each molecule of a substance as soluble as acetic acid is surrounded by water molecules, so that these and the acetic acid molecules are packed in the surface layer alternately, each acetic acid molecule being surrounded by a definite number of water molecules. The CH_3 groups in the acetic acid molecule undoubtedly come to the surface but cover only a part of the surface.

Szyszkowski[1] measured the surface tensions of aqueous solutions of propionic, butyric, valeric and caproic acids (in each case both the normal and the iso compound) and found that results could be accurately expressed by the empirical relation

$$\frac{\gamma}{\gamma_0} = \mathrm{I}-\mathrm{B}\log_{10}\left(\frac{c}{\mathrm{A}}+1\right). \qquad (3)$$

Here γ is the surface tension of the solution while γ_0 is that of pure water, c is the concentration of the fatty acid in mols per liter. A and B are constants.

Szyszkowski found that the constant B was the same for all the fatty acids studied, its numerical value being 0.411. A was a constant for any one substance, but its value decreased rapidly as the length of the hydrocarbon chain increased as follows:

TABLE II

	A Mols per liter	Ratio
Propionic acid	0.165	3.25
Butyric acid	0.051	3.40
Valeric acid	0.0150	3.48
Caproic acid	0.0043	

The iso-compounds gave practically the same results as the normal. No reason is given by Szyszkowski for the constancy of B or the changes in A. If we deal with rather concentrated solutions so that c is large compared to A then in Equation (3) we may neglect unity in comparison with c/A. Under these conditions γ is a linear function of the logarithm of c. This is the relation found for acetic acid by Milner, and according to Gibb's equation this must mean that the amount of fatty acid adsorbed in the surface is independent of the concentration.

By differentiating (3) we obtain

$$d\gamma = -0.434\mathrm{B}\gamma\frac{dc}{c+\mathrm{A}}. \qquad (4)$$

[1] *Z. physik. Chem.* **64**, 385 (1908).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Substituting this in (1) yields

$$q = \frac{0.434 B \gamma_0}{RT} \frac{c}{c+A}. \tag{5}$$

This equation shows us that for very dilute solutions (c small compared to A) the amount adsorbed in the surface is proportional to the concentration and is equal to

$$q = \frac{0.434 B \gamma_0}{RT} \frac{c}{A}. \tag{6}$$

The amount adsorbed increases more slowly than the concentration, and finally when c is large compared to A, the surface becomes saturated. The limiting amount adsorbed is then

$$q_\infty = \frac{0.434 B \gamma_0}{RT}, \tag{7}$$

Since B was found to be the same for different fatty acids, the number of molecules adsorbed per unit area must be the same. If we multiply q_∞ by N (the Avogadro number), we obtain the number of molecules per sq. cm. The reciprocal of this gives us a_s, the area covered by each molecule when the surface is saturated. We thus find

$$a_s = \frac{I}{N q_\infty} = \frac{RT}{0.434 N B \gamma}. \tag{8}$$

Taking $R = 83.2 \times 10^6$, $N = 6.06 \times 10^{23}$, $T = 293°$ and $\gamma_0 = 72.5$.

$$a_s = \frac{12.8 \times 10^{-16}}{B}. \tag{9}$$

Substituting the value $B = 0.411$ found by Szyszkowski we obtain $a_s = 31 \times 10^{-16}$ sq. cm per molecule. This value comes reasonably close to the value $a_0 = 21.5 \times 10^{-16}$ found for the higher fatty acids by the study of the films on water. The fact that a_s has the same value for each of the acids from propionic to caproic shows that in the more concentrated solutions the molecules in the adsorbed surface layer are packed tightly side by side with the hydrocarbon chains arranged vertically.

In the case of very dilute solutions we see from Equation 6 that the different acids are adsorbed in the surface layer in different amounts, these being inversely proportional to the values of A (Table II). The longer the hydrocarbon chain the greater the adsorption from a dilute solution, although with more concentrated solutions the length of the chain is without influence.

These facts are readily explainable by the new theory of surface tension. Let us consider what must be the mechanism of these phenomena. In the surface of a sufficiently dilute solution the molecules of the fatty acid will be so far apart that they do not influence one another. There must be a kinetic equilibrium between the molecules arriving at the surface from the interior and

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

those passing from the surface to the interior. The rate at which the molecules arrive at the surface is proportional to the concentration. The rate at which they pass into the interior is proportional to the number in the surface. For equilibrium in dilute solutions it is evident that the number in the surface must be proportional to the number in the interior. This explains the form of Equation 6 which merely states that q is proportional to c and serves as a definition of the constant A. From the above kinetic considerations, together with the conclusion that a saturated surface layer must consist of a layer one molecule deep, we thus obtain from Gibb's equation, a rational derivation of Szyszkowski's empirical equation.

The potential energy of a molecule of a fatty acid is lower when the molecule is on the surface than when it is in the interior. The rate at which molecules pass from the interior to the surface depends primarily on the concentration of the solution, but not on the difference of potential energy between the molecules in the interior and on the surface. The rate at which the molecules pass from the surface back to the interior depends on the number of molecules in the surface, but is also dependent to a very great degree on the difference in the potential energy of the molecule in the two states. The phenomena is quite analogous to evaporation. The manner in which *m* the "rate of evaporation" of the molecules from the surface into the interior of the liquid, varies with the difference of potential energy may be calculated from Maxwell's distribution law[1].

Taking into account the kinetic equilibrium between the surface layer and the interior of the solution it may be readily shown that the following relation should hold between the amount adsorbed in the surface and the concentration in the solution:

$$\frac{q}{c} = \mathrm{K}e^{\lambda/\mathrm{RT}}. \tag{10}$$

Here λ is the decrease in potential energy which occurs when a gram molecule of the dissolved substance passes from the interior of the solution into the surface layer. K is a constant.

We may now apply this equation to the case of a series of solutions of homologous compounds. If λ increases in arithmetical proportion as we pass from one member of the series to the next, then according to (10) the ratio q/c will increase in geometrical proportion. By Equation 6, q/c is inversely proportional to A, the constant tabulated in Table II. Combining Equations 6 and 10 we obtain for any two members of a homologous series

$$\frac{\mathrm{A}}{\mathrm{A}'} = e^{\lambda'-\lambda/\mathrm{RT}}. \tag{11}$$

---

[1] For further details see Equation 5 and the references given in the footnote on page 33 of Part I of this paper *J. Am. Chem. Soc.* **38**, 2221 (1916)).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Now the experimental data of Table II show that A decreases in a constant ratio each time a CH_2 group is added to the hydrocarbon chain. Taking this ratio to be 3.4 and substituting in Equation II gives $\lambda' - \lambda = 2.98 \times 10^{10}$ ergs per gram molecule or 710 g calories per mol. We may thus conclude from the experimental data that each CH_2 added to the hydrocarbon chain of a fatty acid increases the potential energy λ in very dilute solutions by the constant amount of 710 calories per gram molecule. This must mean that each CH_2 added occupies a similar position, in regard to the structure of the surface layer, as the CH_2 groups already present. Since the range of the forces involved is small compared to the size of the molecule, it must therefore follow that each CH_2 group in these dilute solutions forms a part of the surface. In other words, the hydrocarbon chain lies spread out flat on the surface of the water. As the concentration of the solution increases, the molecules become more closely packed in the surface layer, and finally when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically.

We have seen in the case of the higher fatty acids that the surface films have no appreciable effect on the surface tension until their molecules are packed tightly. With the saturated fatty acids they must even be packed so that they stand vertically on the surface before affecting the surface tension. The lower fatty acids on the other hand change the surface tension considerably even when the number of molecules on the surface is very much less than enough to cover the surface with a single layer.

We have seen in the derivation of Equation (6) that for dilute solutions of fatty acids q is proportional to c. From Equation 1 this means that $d\gamma/dc$ is constant, or in other words γ is a linear function of c. We may therefore place

$$-\frac{d\gamma}{dc} = \frac{\mathrm{F}}{c}. \tag{12}$$

where

$$\mathrm{F} = \gamma_0 - \gamma. \tag{13}$$

The number of molecules adsorbed in the surface is $\mathrm{N}q$ so the area per molecule is

$$a = \frac{1}{\mathrm{N}q}. \tag{14}$$

Substituting (12) and (14) in (1) we find

$$\mathrm{F}.\mathrm{N}a = \mathrm{RT}. \tag{15}$$

This equation is exactly analogous to the gas law $p\mathrm{V} = \mathrm{RT}$. The quantity $\mathrm{N}a$ is the area available per gram molecule and corresponds to V. The force F is the force with which the film tends to spread over the surface, and this corresponds to the gas pressure p.

With dilute solutions of the lower fatty acids the adsorbed films thus follow the laws of ideal gases. From the kinetic viewpoint this means that the mole-

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

cules are free to diffuse over the surface and are taking part in the thermal agitation (Brownian movement) just as any gas molecule does. The strips of paper on the surface of the water in the apparatus shown in Fig. 6 correspond to semipermeable membranes which allow the water to pass, but not the substance in the surface film.

The magnitude of the forces due to this gas-like expansion of surface film is by no means small. Thus from Equation 15 we calculate that at 20° the force F would be 4 dynes per cm when $a = 100 \times 10^{-16}$ sq. cm per molecule.

From Fig. 8 we see that in the case of the higher fatty acids the films do not spread upon the surface in the way required by Equation 15. Thus with palmitic acid the force F falls to less than 0.2 dyne per cm when $a = 23 \times 10^{-16}$ sq. cm, whereas by (15) the force should be 17.5 dynes per cm for this value of a[1].

This means that the film no longer behaves like a gas, but rather as a liquid or solid. Adsorbed films in the surfaces of liquids may thus exist in three distinct conditions corresponding to the solid, liquid, and gaseous states. It is to be expected that the transition from gaseous to liquid films may be either continuous (as in the case of the lower fatty acids), or discontinuous (higher fatty acids), and that under proper conditions, phenomena quite analogous to the critical phenomena of gases should be observed.

Any solid or liquid film must have a certain tendency to spread on the surface by giving off separate molecules which will follow the gas laws. This tendency may be measured as a "surface-vapor-pressure." With palmitic acid and higher fatty acids this pressure is less than 0.1 dyne per cm. The smallness of this pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapor phase and from going into solution in the water. There are thus intimate relationships between the lowering of surface tension produced by fatty acids and the vapor pressures and solubilities of these substances. These relationships will be discussed in more detail in another part of this paper.

When the solubility or vapor pressure of a surface film is not negligible the paper strips of the apparatus shown in Fig. 6 are no longer equivalent to semipermeable membranes, so that this method fails. It will probably be possible by means of Gibbs' Equation 1 or a more accurate equation of similar

---

[1] To measure the relation between a and F for very small values of F a special balance like that of Fig. 6 but of greater sensitiveness was constructed. By also using a weaker air blast it was possible to increase the sensitiveness many fold, so that a force of 0.05 dyne per cm could be measured with certainty. Until the force F decreases to about 0.4 dyne per cm or less the curves shown in Figs. 8–18 approach the horizontal axis, forming a definite angle with it, instead of approaching it asymptotically. For still weaker forces (0.05 to 0.3 dyne per cm) a transition curve asymptotic to the horizontal axis was sometimes observed, but this appeared to be due to some contamination of the water surface rather than to the substances investigated.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

type, to study the relations between F and a during the transition from the state of liquid films to that of "gaseous" films.

Before discussing in more detail the mechanism of adsorption in the surfaces of liquids, let us consider some additional experimental data on the surface tension of solutions.

The surface tensions (at 15°) of a large number of aqueous solutions of organic substances have been accurately determined by J. Traube[1]. His results are given in a form which renders them particularly adapted to our present purposes. In each case he measured the surface tensions of solutions of the following concentrations: 1, 0.5, 0.25, 0.125, etc., gram molecules per liter. He continued diluting each solution until the surface tension became nearly equal to that of pure water. In some cases it was necessary to dilute to 1/1024 mols per liter. Traube drew the following general conclusions from his work on organic substances containing hydrocarbon chains with a single active group (acids, alcohols, esters, amines, and aldehydes):

1. For very dilute solutions the depression of the surface tension $\gamma_0 - \gamma$ (or F) is proportional to the concentration. In other words F/c is constant.

2. The ratio F/c for dilute solutions increases about threefold for each CH_2 added to the hydrocarbon chain in the molecules.

3. As the concentration of the solution increases F ceases to be proportional to c, but increases more slowly than c.

4. The concentration at which F ceases to be proportional to c is lower the greater the length of the hydrocarbon chain.

5. At still higher concentrations F increases by constant increments (about 8.0 dynes per cm), each time the concentration is doubled. That is, the surface tension decreases in arithmetical proportion while the concentration increases in geometrical proportion.

6. The depression of the surface tension F is expressed as a function of the concentration c by the following equation:

$$F = f(c/A) \tag{16}$$

Here A is a constant characteristic of each substance and f represents a function which is the same for all substances.

Traube explained the first of the above conclusions by kinetic considerations much as has been done in this paper. He either did not attempt to explain the other relations or he gave explanations which at present are of little value.

It is interesting to note that in the above conclusions Traube anticipates by 16 or 17 years most of the relations found by Milner and by Szyszkowski. The present theory of the structure of the surface layer furnishes a rational explanation of each of Traube's conclusions.

---

[1] *Ann.* **265**, 27–55 (1891).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Traube's results can be expressed fairly well by Szyszkowski's Equation 3. This equation may be written in the form

$$F = B\gamma_0 \log\left(1 + \frac{c}{A}\right). \tag{17}$$

For very dilute solutions, where c/A becomes small compared to unity the ratio F/c becomes constant and equal to

$$\left(\frac{F}{c}\right)_0 = \frac{0.434\ B\gamma_0}{A}. \tag{18}$$

On the other hand for concentrated solutions where c/A is large compared to unity, Equation (17) reduces to

$$F = B\gamma_0 \log c - \text{constant}. \tag{19}$$

Traube usually started with a gram-molecular solution repeatedly doubling its volume so that the molecular volume V was increased through the steps 1, 2, 4, 8, 16, etc. The value of F at first decreased by more or less constant increments — ΔF. But as the solution became more dilute ΔF became approximately proportional to c as would be expected by Equation (18). For concentrated solutions where Equation (19) still holds, we thus obtain

$$\Delta F = B\gamma_0 \log 2. \tag{20}$$

Substituting $\gamma_0 = 72.95$, we get

$$B = 0.0454\ \Delta F. \tag{21}$$

In attempting to calculate B from Traube's data it was found that the range of concentration was usually not quite sufficient to allow Equation 21 to be applied with accuracy.

The equation actually used in calculating B was obtained by expanding (17) into a series and combining the result with (18) and (21) as follows:

$$B = 0.0454\ \Delta F\left(1 + \frac{\Delta F}{(cF/c_0)}\right) \tag{22}$$

The correction term in the second member usually amounts to less than 10%.

Similarly it was found that the values F/c given by Traube did not quite reach a constant value as the solutions were diluted. An extrapolation formula based on an expansion of (17) was also developed for this case.

$$\left(\frac{F}{c}\right)_0 = \frac{F}{c}\left(1 + \frac{F}{63B}\right). \tag{23}$$

Here B was first calculated by (22).

Table III contains values of B and $(F/c)_0$ calculated for a large number of substances from Traube's data. The first column gives the range in the molecular volumes V of the solutions used by Traube. The second gives

Digitized by Google Original from UNIVERSITY OF MICHIGAN

values of $(F/c)_0$ calculated by Equation (23). The next column gives values of B by (22). In some cases the maximum concentration used by Traube was not sufficient to yield a saturated surface. This was shown by a marked lack of constancy in the values of ΔF for the higher concentrations. In such cases the value of B could not be determined, or at most only a lower limit for B could be found.

TABLE III

Substance	Range of V	$(F/c)_0$	B	λ_{obs}	λ_{cal}	$a_s \times 10^{-16}$ sq. cm
Formic acid HCOOH	1—8	8.0	..	1078	1062	..
Acetic acid CH_3COOH	1—16	27.0	..	1710	1697	..
Propionic acid C_2H_5COOH	1—64	77.0	0.37	2290	2312	33.9
Butyric acid C_3H_7OOH	1—128	230.0	0.40	2910	2937	31.2
Iso-butyric acid C_3H_7COOH	1—128	240.0	0.40	2940	2937	31.2
Iso-valeric acid C_4H_9COOH	4—256	720.0	0.41	3570	3562	30.5
Methyl alcohol CH_3OH	1—8	11.0	..	1240	1200	..
Ethyl alcohol C_2H_5OH	1—16	33.0	0.39	1820	1825	32.0
Propyl alcohol C_3H_7OH	1—32	98.0	0.43	2430	2450	29.1
Iso-propyl alcohol C_3H_7OH	1—32	96.0	0.36	2430	2450	34.7
Iso-butyl alcohol C_4H_9OH	1—64	310.0	0.45	3080	3075	27.8
Iso-amyl alcohol $C_5H_{11}OH$	4—128	910.0	0.45	3700	3700	27.8
Methylacetate CH_3COOCH_3	1—32	85.0	0.42	2340	2345	29.8
Propyl formate $HCOOC_3H_7$	4—128	250.0	..	2960	2970	..
Ethyl acetate $CH_3COOC_2H_5$	2—128	270.0	0.42	3000	2970	29.8
Methyl propionate $C_2H_5COOH_3$	2—128	245.0	0.44	2950	2970	28.4
Propyl acetate $CH_3COOC_3H_7$	8—256	840.0	>0.41	3650	3595	30.5
Ethyl propionate $C_2H_5COOC_2H_5$	8—256	745.0	>0.41	3580	3595	30.5
Propyl propionate $C_2H_5COOC_3H_7$	32—1024	2050.0	>0.37	4160	4220	33.8
Allyl acetate $CH_3COOC_3H_5$	8—256	470.0	>0.42	3320	3195	29.8
Allyl alcohol C_3H_5OH	1—32	46.0	0.44	2000	2050	28.4
Allyl amine $C_3H_5NH_2$	1—32	51.0	0.31	2060	2075	38.4
Propyl amine $C_3H_7NH_2$	1—32	110.0	0.35	2490	2475	34.0
Butyl aldehyde C_3H_7CHO	2—64	160.0	0.48	2710	2710	24.8
Oxy-butyric acid $C_3H_6(OH)COOH$	2—32	53.0	0.25	2080	2137	47.7
Acetone $CH_3CO.CH_3$	1—32	62.0	0.28	2170	2170	42.5
Dimethyl-ethyl carbinol $(CH_3)_2(C_2H_5)OH$	2—256	590.0	0.33	3450	3450	36.1
Paraldehyde $C_6H_{12}O_3$	2—64	240.0	0.42	2940	..	28.4
Glycol $(CH_2OH)_2$	1—8	2.4	..	563	550	..
Acetamide CH_3CONH_2	1—8	3.8	..	740	740	..
Oxalic acid $(COOH)_2$	4—8	2.1	..	516	550	..
Methyl oxalate $(COOCH_3)_2$	4—32	36.0	..	1870	1800	..
Malonic acid $CO_2H.CH_2.CO_2H$	4—8	12.0	..	1280	1175	..
Succinic acid $CO_2H.CH_2.CH_2.CO_2H$	4—8	18.5	..	1510	1800	..
Maleic acid $CO_2HCH:CHCO_2H$	4—32	8.3	..	1090	1400	..
Fumaric acid $CO_2H.CH:CH.CO_2H$	32	11.5	..	1260	1400	..
Malic acid $CO_2H.CH_2.CHOH.CO_2H$	4—8	6.0	..	940	1000	..
Tartaric acid $CO_2H(CHOH)_2CO_2H$	1—8	0.5	..	172	200	..

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

From the values of $(F/c)_0$ we can calculate λ the loss in potential energy when a gram molecule of the solute passes from the interior to the surface of the solution. We have previously shown from Szyszkowski's data how the increase in λ for each CH_2 could be determined. To estimate the approximate absolute value of λ we may proceed as follows:

It is shown in works on the kinetic theory[1] that for a state of equilibrium the distribution of a gas between two regions in which the potential energy is different, is given by the relation

$$\frac{c}{c'} = e^{-\lambda/RT}. \tag{24}$$

Here c and c_1 are the respective concentrations in the two regions and λ is the difference in potential energy per gram molecule.[2]

For solutions so dilute that F/c is constant, we may expect Equation 24 to be applicable and we may thus use it to calculate the concentration c in the surface layer in terms of λ or vice versa.

The equation may also be derived from purely thermodynamical principles.

If λ is expressed in calories, Equation (24) may be written

$$\lambda = RT \ln \frac{c_1}{c} = 4.57T \log \frac{c_1}{c}. \tag{25}$$

This equation is similar in form and analogous in meaning to Nernst's equation of the electromotive force of reversible cells.

The amount of solute q adsorbed in the surface layer per sq. cm may be roughly taken to be

$$q = \frac{\tau(c_1 - c)}{1000}, \tag{26}$$

where τ is the thickness of the surface layer in which adsorption takes place.

Combining Gibbs' Equation (1) with (12) we obtain

$$q = \frac{c}{RT}\left(\frac{F}{c}\right). \tag{27}$$

Eliminating q from (26) and (27) and combining with (25) gives for dilute solutions

$$\lambda = 4.57T \log\left[1 + \frac{1000}{\tau RT}\left(\frac{F}{c}\right)_0\right]. \tag{28}$$

---

[1] For example Jean's, *Dynamical Theory of Gases*, p. 78.

[2] The above equation is closely related to Boltzmann's conception, according to which entropy is equal to the logarithm of the probability. The ratio between the probability that a molecule will be in the interior, and the probability that it will be in the surface is thus proportional to $e^{-\Phi}$ where Φ is the entropy. The quantity λ/RT corresponds to the entropy.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Taking T = 288 and assuming $\tau = 6\times10^{-8}$ cm this equation reduces to

$$\lambda = 1318 \log\left[1+0.695\left(\frac{F}{c}\right)_0\right]. \tag{29}$$

This equation was used for calculating the values of $\lambda_{obs.}$ given in Table III. The choice of the particular value of τ to use in (28) is somewhat arbitrary, but since the molecules adsorbed in the surfaces of these dilute solutions lie flat in the surface it is probable that τ is of the same order of magnitude as the values found for ricinoleic acid or triricinolein, namely, 4.7×10^{-8}.

The last column of Table III gives the values of A calculated from B by an equation similar to (9) except that the numerical constant was 12.5 instead of 12.8, since the temperature in Traube's experiments were 15° instead of 20°.

It is seen from the table that $\lambda_{obs.}$ increases on the average by about 625 calories for each CH_2 added to the molecule. This means that λ can be expressed in general by an equation of the form

$$\lambda_{cal.} = \lambda_0 + 625\, n, \tag{30}$$

where n is the number of carbon atoms in the molecule. The quantity λ_0 has a different value for each type of substance as is shown in Table IV.

TABLE IV

Values of λ_0

Type	Formula	λ_0
Tertiary alcohol	R_3COH	950
Primary amine	RCH_2NH_2	600
Primary alcohol	RCH_2OH	575
Ester	RCOOR′	470
Monobasic acid	RCOOH	437
Ketone	RCOR′	295
Aldehyde	RCHO	210
Amide	$RCONH_2$	−510
Dibasic acid (or alcohol)	....	−700

When a double bond is present in the molecule the value of λ_0 is decreased by about 400. The addition of one or more hydroxyl groups to a mono- or dibasic acid decreases λ_0 by about 800 for ach hydroxyl group.

The fifth column of Table III gives values of $\lambda_{cal.}$ which have been calculated by Equation 30, using the values of λ_0 in Table IV.

An examination of Table IV shows that λ_0 becomes smaller as the active groups in the molecule become more polar in character. It also shows that the polar character is not additive. Two active groups attached to adjacent carbon atoms, as in glycol, cause a very great decrease in λ_0. Such effects,

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

with which chemists are familiar, are undoubtedly due to forces transmitted from atom to atom in the group molecule. It is probable that these forces are caused by a displacement in the relative positions of the electrons and positive nuleci. Thus if an oxygen atom is combined with a carbon atom at one end of a hydrocarbon chain the electrons in the carbon atom are probably displaced towards the oxygen atom and the positive nulecus of the carbon atom displaced away from the oxygen atom. This displacement causes a similar but smaller displacement of the electrons of the next carbon atom and so on.[1]

The close agreement between the observed and calculated values of λ in Table III shows that, except in the case of active groups in close proximity within the molecule, the change in potential energy λ between the interior and surface of the liquid is an additive property.

The results for a_s in Table III are in substantial agreement with the results previously discussed. For the saturated acids, alcohol, and esters the values are approximately the same (30×10^{-16} sq. cm) and are independent of the number of carbon atoms.

The presence of double bonds (allyl alcohol and acetate) does not seem to cause any increase in a_s, probably because these are forced away from the water before the surface becomes saturated. With oxy-butyric acid a_s is much greater (48×10^{-16}), indicating that the hydroxyl group is in contact with the water even when the surface is saturated. The large value for acetone (42.5) and the small value for butyl aldehyde (24.8) are noteworthy, but until verified by other data it would hardly be safe to draw conclusions from these differences.

There are many other data available from which the arrangement of group molecules in surface layers are determinable. Some of these will be briefly mentioned.

Morgan and Egloff[2] give the surface tensions of solutions of phenol and water three temperatures. From these data by Equation 1 the amounts of phenol adsorbed per sq. cm (q) may be calculated.

It is found that with increasing concentration q increases, rapidly at first, then more slowly until it reaches a maximum of about 48×10^{-11} g molecules per sq. cm, showing that the surface becomes saturated with phenol molecules. This maximum value of q is approximately the same at all three temperatures (0°, 35° and 65°), but at the higher temperatures it requires a greater concentration of phenol in the solution to give a saturated surface than at lower temperatures. This fact is a natural result of the kinetic agitation which tends to equalize the concentration in the surface and in the solution. From the above value of q it can be readily calculated that the area per molecule

---

[1] Effects of this kind are probably of importance not only in organic chemistry, but in the study of the structure of the surfaces of crystals and of liquids. In some cases such phenomena may cause adsorbed layers to be more than one group molecule in thickness.

[2] *J. Am. Chem. Soc.* **38**, 844 (1916).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of adsorbed phenol is $a_0 = 34 \times 10^{-16}$ and the thickness of the film is $\tau = 4.3 \times 10^{-8}$ cm. These results would seem to indicate that the phenol molecules in the surface of an aqueous solution lie flat on the surface, and that the diameter of the disk-shaped (assumed) molecule is about one and a half times its thickness.

Morgan and Egloff's data on triethyl amine-water solutions show that the surface is saturated with this substance even with the most dilute solutions used (0.5%). The values of q were fairly constant $q = 40 \times 10^{-11}$ and were the same at 0° as at 30°. This result corresponds to

$$a_0 = 41 \times 10^{-16} \text{ sq. cm}$$
$$\tau = 5.6 \times 10^{-8} \text{ cm.}$$

It is probable from these results that the three ethyl groups lie spread out upon the surface while the nitrogen atom is below the surface and is surrounded by water molecules combined with it by secondary valence.

Worley[1] gives data for aqueous solutions of aniline at several temperatures from 15° to 75°. The values of q calculated from (1) show a variation quite similar to that found from the data on phenol-water solutions. The surface becomes saturated more easily at low than at high temperatures. The data are apparently not as accurate as those of Morgan and Egloff, but they indicate a fairly constant saturation value of $q_s = 45 \times 10^{-11}$. This corresponds to

$$a_0 = 37 \times 10^{-16} \text{ sq. cm}$$
$$\tau = 4.0 \times 10^{-8} \text{ cm.}$$

Evidently the arrangement of the aniline molecules in the saturated surface is about the same as that of the phenol molecules.

We have thus far considered cases where the solute is adsorbed in the surface layer, so that the surface tension is less than that of the pure solvent. When inorganic salts are dissolved in water or alcohol the surface tension increases. The surface of the solution thus contains an excess of the solvent. In general we should expect the surface of any liquid to consist of molecules or atoms arranged in a rather definite manner different from that in the interior. If the molecules or atoms of the dissolved substance are surrounded by fields of force strong compared to those of the solvent then it is improbable that the solute molecules will be able to displace solvent molecules in the surface. Hence the surface layer should consist of a single layer of molecules of the solvent from which solute molecules are excluded.

From Gibbs' Equation 1 we see that if the surface tension *increases* linearly with the concentration, there is a *deficiency* of the solute in the surface layer which is proportional to the concentration. Now this is exactly what we should

[1] *J. Chem. Soc.* (London) **105**, 260 (1914).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

expect if the surface layer consists of pure solvent. Let τ be the thickness of this layer. Then q the deficiency of solute per sq. cm of surface is

$$q = \frac{\tau c}{1000}$$

or by (1)

$$\tau = 1000 \frac{-q}{c} = -\frac{1000}{RT} \frac{d\gamma}{dc}. \qquad (31)$$

We can thus calculate τ the thickness of a single layer of molecules of the solvent by measuring the increase of surface tension produced by the addition of a soluble salt.

Unfortunately the data for $d\gamma/dc$ for acqueous salt solutions are rather variable. Thus for potassium chloride solutions different observers have found results given in Table V

TABLE V

Observer	$d\gamma/dc$	τ cm	a sq. cm
Forch[1]	1.41	3.3×10^{-8}	9.0×10^{-16}
Whatmough[2]	1.81	4.24×10^{-8}	7.02×10^{-16}
Linebarger[3]	1.75	4.1×10^{-8}	7.26×10^{-16}
Quincke[4]	1.747	4.1×10^{-8}	7.27×10^{-16}
Volkman[5]	1.56	3.66×10^{-8}	8.15×10^{-16}
Rother[6]	1.63	3.83×10^{-8}	7.80×10^{-16}

The values of τ were calculated from Gibbs' equation by (31), taking into account the electrolytic dissociation of the potassium chloride solution. This is best done by using Lovelace, Frazer and Miller's data[7] on the vapor pressure of potassium chloride solutions and then applying Gibbs' equation in the form

$$q = \frac{-p}{RT} \frac{d\gamma}{dp}, \qquad (32)$$

where p is the vapor pressure of the solution. By substituting values of q obtained in this way into (31) the values of τ given in Table V were found.

From these results it may be concluded that the layer of pure water adsorbed in the surface of a potassium chloride solution is about 4×10^{-8} cm thick.

---

[1] Forch, *Ann. Phys.* [4] **17**, 744 (1905).
[2] Whatmough, *Z. physik. Chem.* **39**, 154 (1901).
[3] Linebarger, *J. Am. Chem. Soc.* **21**, 413 (1899).
[4] Quincke, *Ann. Phys.* [2] **160**, 337, 560.
[5] Volkman, *Ibid.* [3] **11**, 177; **17**, 353 (1881).
[6] Rother, *Ibid.* [3] **21**, 576 (1884).
[7] *J. Am. Chem. Soc.* **38**, 515 (1916).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

This probably represents the length of the water molecules in the surface, so that their cross-section (assuming H_2O as the group molecule) is about 7.4×10^{-16} sq. cm.

It is interesting to note that the results obtained with other salts are in substantial agreement with the above. Although different salts give different values of $d\gamma/dc$, these differences seem to be almost wholly accounted for by differences in the degree of electrolytic dissociation.

Cederberg[1] finds for solutions of sodium iodide in ethyl alcohol $d\gamma/dc = 1.09$. This leads to $\tau = 4.4\times10^{-8}$ cm and $a = 22\times10^{-16}$ sq. cm for the adsorbed layer of pure alcohol in the surface of this solution.

Gibbs' equation may also be applied to cases where the surface tension of a liquid is decreased by the presence of a vapor above the liquid. For example, benzol or hexane vapors brought into contact with the water decrease the surface tension of the water very markedly. By measuring the surface tension as a function of the partial pressure of the vapor up to pressures sufficient to yield a saturated adsorbed film, it must be possible to obtain very definite information as to the shapes and arrangements of these hydrocarbon molecules. Experiments of this kind were begun in this laboratory, but owing to the present unsettled conditions have been discontinued.

Adsorption of Liquids by Solids

The heats of adsorption of various organic liquids when brought into contact with Fuller's earth, bone charcoal, or kaolin, have been carefully studied by Gurvich[2] in an investigation of the nature of the forces involved in adsorption. Gurvich traces relationship between this heat of adsorption and such properties as chemical reactivity, solubility, latent heat of evaporation, dielectric constant, "internal pressure", and surface tension, explaining these relationships in terms of his previously mentioned theory of "physicochemical forces".

The results of his determinations of the heats of adsorption are given in Table VI. These are the heats in small calories, liberated when 1 g of the adsorbent is added to a relatively large quantity of the liquid in a calorimeter.

Gurvich remarks:

"A glance at this table shows that with all three absorbents, most heat is evolved when compounds with double bonds or those containing oxygen or nitrogen are used; and the least heat is generated by saturated hydrocarbons or such saturated compounds as carbon disulfide

---

[1] *J. chim. phys.* **9**, 10 (1911).

[2] L. G. Gurvich, *J. Russ. Phys. Chem. Soc.* **47**, 805–27 (1915). As this excellent paper is in the Russian language, and has been especially translated for me, it may be worth while to give here Gurvich's results in some detail, especially since they have a very intimate bearing on my theories of the constitution of solids and liquids.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

or tetrachloride. The substances which are most active chemically exhibit the most intense attraction for the absorbents.

"The most natural conclusion from this fact would be that in adsorption we have to do with rather unstable molecular compounds. It would seem that Werner's theory of secondary valence would thus find further confirmation; *but further experiments have proved that this is not so.*"

Gurvich rejects the theory that these phenomena are the result of chemical forces for the following three reasons.

TABLE VI

Heat of Adsorption

Substance	Fuller's earth	Bone charcoal	Kaolin	Volume adsorbed from saturated vapor by 1 g. of Fuller's earth, cc.	Dispersive power %
Amylene	57.1	..	78.8	...	1.54
Water	30.2	18.5	..	0.683	2.82
Acetone	27.3	19.3	..	0.684	1.72
Methyl alcohol . . .	21.8	17.6	27.6	0.679	1.60
Ethyl acetate	18.5	16.5	..	0.636	1.05
Ethyl alcohol	17.2	16.5	24.5	...	..
Aniline	13.4	..	..	...	..
Amyl alcohol	10.9	10.6	20.4	...	..
Ethyl ether	10.5	..	..	...	0.90
Chloroform	8.4	14.0	15.7	0.611	0.86
Benzene	4.6	11.1	9.9	0.610	0.39
Carbon disulfide . .	4.6	8.4	9.9	0.621	..
Carbon tetrachloride .	4.2	13.9	9.4	0.625	0.27
Hexane	3.9	8.9	7.2	...	0.22

1. He finds that amounts of different liquids adsorbed by a given amount of absorbent are not in agreement with stoichiometric relations. Instead, he finds that the *volumes* of the different substances adsorbed are very nearly equal. In these determinations he placed 1 g of the absorbent in a Hempel exsiccator in presence of the *saturated vapor* of the liquid until the weight became constant, which required from 15–25 days. The results thus obtained with Fuller's earth are given in the fourth column of Table VI. The volumes of liquid adsorbed from the vapor thus vary over only the relatively small range from 0.61 to 0.684, cc. per g. The number of gram molecules adsorbed per 100 g of Fuller's earth, however, vary from 0.65 for CCl_4 up to 3.79 for H_2O.

2. From experiments, and by reference to work of other investigators he concludes that the range of the forces causing adsorption and the other

Digitized by Google Original from UNIVERSITY OF MICHIGAN

phenomena considered, is always of the order of 3×10^{-6} cm. He experimented with silver foil and glass wool in *saturated vapors* of CCl_4, CS_2 and ethyl acetate. The absorbents were placed in six glass tubes within the exsiccator, and the increase in weight in 20 hours was determined. No further increase occurred in an additional 22 hours. The silver foil had a surface of 4150 sq. cm while the glass wool (threads 0.018 mm diameter), had a surface of 2250 sq. cm. By calculation from the increases in weight, (20–50 mg) the "thickness" of the adsorbed film, in the six cases studied were found to lie within the range between 2.6 and 3.5×10^{-6} cm.

Gurvich refers to results of similar magnitude obtained by Magners for the adsorption of SO_2 by glass, by Shapin for adsorption of CO_2, NH_4OH, etc., by glass, and by Parks for the adsorption of water vapor by glass. Quincke, Reinold and Ruecker, Moro, Wensam and others have obtained results of the same order of magnitude by entirely different methods.

Gurvich concludes:

"It seems to me, therefore, very probable that the physico-chemical force of attraction *in all its manifestations, is* not *limited* to adjacent molecules, but reaches out upon a large number of more distant molecules, its influence gradually decreasing as the distance from the center increases.[1]

"The action of the force of chemical affinity involved in the formation of compounds according to more or less simple stochiometric proportions, is limited to distances of atomic order, or, at most, to distances separating neighboring molecules. The sphere of action of physico-chemical forces is many times greater.

3. "Finally, the third distinction between physico-chemical and purely chemical forces is the following:

"The heat of reaction between any two elements, generally speaking, is the greater, the more dissimilar the elements are. In the action of the residual chemical energy (physico-chemical forces) we see just the reverse; hydrocarbons and their immediate derivations generate much more heat (see Table VI) with charcoal than with Fuller's earth or kaolin; alcohols and in general oxygen compounds act in just the reverse manner. In the study of solubility it was noted long ago that chemically similar substances dissolve one another more easily than dissimilar substances."

Gurvich gives these three reasons as convincing proof that adsorption phenomena are not the result of purely chemical forces. The heat of adsorption is, however, in some way, clearly related to the chemical properties. This is due he thinks "to some residual energy in the chemical molecule intermediate in character between chemical and physical". This residual energy differs from the purely chemical in the three ways given above but it also differs essentially from the potential energy of purely physical attraction by its specific action or "specificity".

---

[1] These views of Gurvich are cited here at such length because they appear to be the prevalent views among workers in this field. The insufficiency and unreliability of the data upon which these views are based are typical of nearly all the data upon which the general distinction between "physical" and "chemical" forces usually rests.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

In discussing the relation between these "physico-chemical" forces and "true chemical forces" Gurvich points out that chloroform, which is chemically more active than carbon tetrachloride, has the higher heat of adsorption (Table VI). Among the alcohols there is a parallelism between the heat of adsorption and the velocity of esterification and also the heat liberated during the formation of complex compounds with magnesium propyl iodide.

Gurvich observes that when Fuller's earth is shaken up with hexane it settles out rapidly, leaving a nearly clear liquid, but with acetone the liquid remains turbid. The disintegration of the Fuller's earth by acetone can even be observed under the microscope. By determining the percentage of the Fuller's earth which remains in suspension in different liquids he determines the dispersive power as given in the last column of Table VI. The closeness of the parellism between this phenomena and the heat of adsorption is very striking.

The disintegration of the Fuller's earth by these liquids is looked upon as entirely analogous to the solubility of substance in a liquid, except that the particles in the latter case are smaller. In fact there is a rather close parallelism between the solvent power of the liquids shown in Table VI and the observed heats of adsorption. For example, benzol and unsaturated hydrocarbons are in general better solvents than the saturated. Chloroform is about ten times more soluble in water than is carbon tetrachloride. Benzol mixes in all proportions with methyl alcohol, while only 31% of hexane can be dissolved in this alcohol.

In general the substances with high heats of adsorption have high dielectric constants.

Among closely related chemical compounds Gurvich finds that the substances with the higher heats of adsorption have in general the higher surface tensions, but this parallelism is not nearly as good as in the cases of the properties cited above.

The chemical properties of substances are characterized by their "specificity". Thus we usually cannot predict how a substance A will react toward a substance B merely from a knowledge of the behavior of A and B (separately) towards a third substance C. Certain very general relationships may exist between different classes of substances, but we are not often able to express the chemical properties of a substance in terms of a single constant as for example the gravitational properties of a body can be expressed by the mass, or the electrical properties by the electric charge.

Gurvich considers that this "specificity" is a sufficient to establish a close relationship between "molecular" and "chemical energy", but for the reasons already given he feels compelled to class the molecular forces as physico-chemical. As illustrating the "specificity" of "molecular processes" he calls attention to the fact "that benzene and hexane liberate twice as much heat

Digitized by Google Original from UNIVERSITY OF MICHIGAN

(Table VI) with charcoal as with Fuller's earth, but acetone, ether and alcohols yield on the contrary more with Fuller's earth than with charcoal".

From the viewpoint adopted in the present paper the forces involved in adsorption, surface tension, etc., are strictly chemical in nature, that is, that do not differ in any essential respect from the forces causing the formation of typical chemical compounds. Let us see how this theory can be reconciled with Gurvich's experimental results.

Consider first the adsorption of a liquid by a plane solid surface. If the molecules of the liquid contain active groups, the molecules will become oriented and will pack into the surface layer in much the same manner as in the case of oil films spread upon the surface of water. In general, there will be a *tendency* for the number of molecules adsorbed to bear a simple integral relation to the number of atoms exposed in the surface of the solid. When the surface is a cleavage plane from a crystal, so that the surface atoms are arranged in a regular lattice, the amounts of different liquids (or gases) needed to saturate the surface would probably frequently stand in stoichiometric relations with each other.

In fact the experiments with oil or adsorbed films on water have already shown that these stoichiometric relations are very common. Thus it was found that the number of molecules of different fatty acids adsorbed per unit area was practically the same for all the acids from propionic up to cerotic. Similarly, the number of molecules of stearic acid per unit area was three times that found for tristearine, etc.

It is evident that the configurations of the adsorbed molecules in general are of great influence in determining the number of molecules that can be adsorbed per unit area. This phenomena is, however, nothing more than *steric hindrance*. In adsorption phenomena, particularly on solid bodies, this steric hindrance must be of very far-reaching significance, much more so for example than in the fields ordinarily covered by organic chemistry.

Suppose we consider the adsorption of two such substances as methyl alcohol and phenol. Since the phenyl group will necessarily occupy more space than the methyl group, the number of molecules of phenol per unit area of a saturated surface will be less than that of methyl alcohol.

We might still expect that the number of phenol molecules would bear a simple relation (such as $\frac{1}{3}$ or $\frac{1}{4}$ to the number of methyl alcohol, but when we take into account the thermal agitation and the kinetic interchange which must occur, it appears more probable that the relative numbers of molecules adsorbed would bear an incommensurate ratio. This would be especially true if instead of a cleavage surface we should give a surface of an amorphous body as absorbent.

Now in the case of porous bodies such as those employed in Gurvich's experiments, there are cavities of nearly all possible sizes and shapes. It is obvious, therefore, that the phenomenon of steric hindrance will become of dominating

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

importance and that even in the case of a series of homologous acids or alcohols we should no longer expect to find stoichiometric relations. For example the number of ethyl alcohol molecules which could attach themselves to the walls of a small cavity would be less than the number of methyl alcohol molecules which could be similarly attached. This difference will become more and more marked as the size of the cavities becomes smaller.

This absence of stoichiometric relationship, therefore, is not to be regarded as evidence that the forces involved are not chemical in nature. It is merely the result of purely geometrical factors. In fact, apart from reactions involving primary valence forces, it seems that stoichiometric relations are the exception rather than the rule, and that where these relations do hold it is merely the result of particularly favorable geometric conditions.

The heat of adsorption is determined in general by the interaction of the active groups and the atoms of the solid body. Thus in Table VI we see that those groups which cause oils, etc., to spread on water surfaces are just those which cause an increase in the heat of adsorption.

Those groups or radicals are the double bond, $-OH$, $= CO$, $-COO-$, $-NH_2-O-$.

The parallelism between these heats of adsorption and the phenomena described in the early part of this paper could hardly be more striking. There can be no reasonable doubt but that the causes of the adsorption are in both cases fundamentally similar.

Let us now consider from the viewpoint of our theory, the three reasons which led Gurvich to decide that these adsorption phenomena are not due to chemical forces.

1. We have already seen that the absence of stoichiometric relationship cannot be taken as a proof of the absence of chemical combination, but that it is simply a result of steric hindrance.

It remains to explain why Gurvich's experiments showed that the *volumes* adsorbed were the same for all the liquids. It must be noted that Gurvich allowed the adsorption to occur in saturated vapor, and that equilibrium was not reached for from 15 to 25 days. Under such conditions every small cavity must fill up completely with liquid because of the decrease of vapor pressure caused by the concavity of the surfaces in the pores of the absorbent. This is a purely secondary phenomenon, being dependent only on the surface tension of the adsorbed liquid, and not on the forces acting between the absorbent and the liquid.

We must picture the processes occurring during the adsorption of, for example, ethyl alcohol by charcoal as follows: The hydroxyl groups of the alcohol are attracted to the carbon atoms, so that as many carbon atoms as possible come into contact (or combine) with the hydroxyl groups. The ethyl groups fill up many of the small cavities, and, in other ways, prevent the hydroxyl groups from coming into contact with the carbon atoms. The larger pores or

Digitized by Google Original from UNIVERSITY OF MICHIGAN

cavities are, however, covered over with a single layer of molecules. When the vapor is *saturated* it is evident that these cavities must also gradually become filled with liquid. But this is to be classed as a capillary phenomena and not as adsorption. It has, for example, nothing to do with the forces acting between the carbon atoms and the hydroxyl groups.

Under these conditions it is only natural that the volume *absorbed* should be about the same for different liquids, since it is simply a measure of the total volume of the larger pores. The amount truly adsorbed is much smaller, and, in the case of the three alcohols given in Table VI, is probably quite accurately proportional to the observed heat of adsorption. The three values, 21.8, 17.2 and 10.9, for methyl, ethyl and amyl alcohols adsorbed by Fuller's earth, indicate how marked is the effect of steric hindrance.

2. Gurvich and many other workers in this field lay a great deal of stress on the supposed fact that the range of the molecular forces is about 3×10^{-6} cm or at any rate is larger than molecular dimensions. According to our theory, however, the range is rather of the order of 10^{-8} cm.

Gurvich experimented with 4150 sq. cm of silver foil in a small tube. This was probably crumpled up loosely and squeezed into the tube. In any case it would be practically impossible to get such a large surface into a tube without having an enormous number of surfaces of contact between adjacent pieces of foil. These capillary spaces in *presence of saturated vapor* or even vapor anywhere near saturation must become filled with liquid held by surface tension and not by adsorption. The same objection may be raised against the experiments with glass wool.

We have seen in Part I (pages 60–62) that other data given in the literature are unreliable for similar reasons.

I have not studied in detail all the references cited by Gurvich as evidence of the large range of molecular forces, but the evidence of a contrary nature which has already accumulated is enough to make me feel confident that the large ranges are only apparent, and are due to secondary causes.

To obtain further information regarding the forces causing adsorption and the thickness of adsorbed films, some experiments have been undertaken for me by Mr. Sweetser. We have used glass, mica, and platinum, with very nearly plane surfaces and have endeavored to reduce the number of contacts between surfaces to a minimum. The pressures used were much below saturation and were usually less than 200 bars. It was found that at 100 bars' pressure the amount of oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide and argon adsorbed on glass or mica at room temperature were not measurable, although if 0.0002 of the surface had been covered by a layer one molecule deep it could have been readily detected. On cooling these surfaces to liquid air temperature the surfaces became covered with a monomolecular layer to the extent of 1 to 10% and at 100 bars' pressure they seemed nearly saturated. The relative amounts of different gases adsorbed were in the same order as

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the boiling points, showing that the forces involved in this adsorption were secondary valence forces such as those involved in the liquefaction of these gases.

With platinum surfaces the phenomena were totally different. Even at pressures below one bar the surface adsorbed hydrogen, carbon monoxide or oxygen immediately to form a layer covering the surface with a layer approximately one molecule (or atom) deep. These films could not be driven off by heating to 360°, but could be made to displace one another. The surfaces were wholly saturated at a few bars' pressure, and no increase in adsorption could be noted by raising the pressure to 200 bars. These films are evidently held to the platinum by primary valence forces.

With the platinum at liquid air temperature the gases are first adsorbed by secondary valence forces, because when the temperature is raised to room temperature the gas first comes off the surface, and then at a temperature somewhat below room temperature goes back again onto the surface.

In no case, however, was any adsorption noted which corresponded to a layer more than one molecule deep.

It is, of course, possible in certain exceptional cases that more than one layer of molecules may be adsorbed on a surface. The tendency of molecules to evaporate from a second layer will in general be somewhat different (either greater or less) than from the surface of the liquid en masse. Such effects may be transmitted from layer to layer because of the orientation of the first layer of molecules, but in most liquids, these effect are probably not transmitted in appreciable degree to more than one or two layers. Effects of this kind would be particularly noticeable with nearly saturated vapors.

From the foregoing considerations we may conclude that the "molecular forces" studied by Gurvich are really chemical forces according to all the tests given by him and that their range of action is not greater than that of other chemical forces.

3. Gurvich's third objection to classing molecular forces as chemical is that they seem most active between similar rather than dissimilar bodies. This objection, however, arises merely from a confusion of secondary and primary valence forces.

In the formation of compounds of the first order we generally find the most marked combining tendencies between strongly electronegative and electropositive elements as for example between the alkali metals and the halogens. This tendency is most readily explained in terms of Lewis' theory.

On the other hand, all through chemistry we find evidence of reactions occurring between substances of similar type, especially where secondary valences are involved. This is shown by reactions between oxides, between halides, between metals, etc., and even by the reactions occurring between various organic compounds. Therefore, the fact that substances of similar character are usually mutually soluble, or that absorbing agents show a preference for

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

chemically related substances, is not be to looked upon as evidence that these phenomena differ in any essential respect from chemical phenomena, but merely as an indication that secondary rather than primary valence forces are involved.

As a final result of this discussion of Gurvich's paper we may conclude that the principles outlined in the beginning of the present paper are applicable to adsorption phenomena in general.

(In the remaining part of this paper surface tension, association, evaporation, freezing, melting, viscosity, solubility, and the internal structure of liquids will be briefly considered.)

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

PART 2

INTERFACIAL PHENOMENA

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE CONSTITUTION OF LIQUIDS WITH ESPECIAL REFERENCE TO SURFACE TENSION PHENOMENA*

Metallurgical and Chemical Engineering
Vol. XV, No. 8, 468, October (1916).

THE EPOCH-MAKING work of Laue and Bragg has given us a clear insight into the structure of crystalline bodies. In the case of inorganic crystalline substances, it has been found that the atoms are arranged according to definite lattices so that certain groups of atoms are repeated in a regular manner. In this arrangement, however, there is nothing to indicate where one group ends and the next begins. Thus, in a crystal of common salt, the chlorine and sodium atoms alternate in regular order, but are not grouped together into pairs. Any division of the crystal into molecules is thus purely arbitrary. We must therefore conclude that solid bodies are not built up of molecules, but of atoms arranged in definite ways; or rather, we should regard a crystal as a single large molecule.

From this viewpoint the forces holding solid bodies together (cohesion, etc.) are chemical forces, and phenomena such as evaporation are strictly chemical phenomena. So far, in the study of crystal structure, only inorganic bodies have been investigated. It is certain that in solid organic bodies the atoms are arranged in groups which are usually identical with the molecules found when the substances exist as vapors. We may call these *group molecules*. There are good reasons for believing that in crystals of an organic substance these group molecules are held together by chemical forces (secondary valence) to form single large molecules.

A similar theory is now proposed for the structure of liquids. Each atom in a liquid is regarded as being chemically combined with all adjacent atoms. This chemical union may in general be of two kinds, characterized by *primary* and *secondary* valences. The atoms held together by primary valence usually constitute *group molecules*, in which the atoms are more or less rigidly attached to each other in definite arrangements. The secondary valence serves to hold the group molecules together. In very many cases (such as most inorganic

---

[EDITOR'S NOTE: It also appears as Chapter Five of the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

* An abstract of a paper read at the New York City meeting of the American Chemical Society, September, 1916, in The Symposium on Colloids.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

liquids) the group molecules are very much simpler than the usual "chemical molecules" and may often be entirely absent. Thus, in such substances as water, concentrated sulphuric acid or in molten salts or metals, there are probably no group molecules at all; the atoms being held together by secondary valences.

A drop of liquid is thus regarded as a single large molecule. In fact, the whole earth, including the oceans (but excluding the atmosphere) may be looked upon as a single molecule.

The most essential difference between liquids and solids is the mobility of the former. The chemist is already familiar with a mobility between different parts of a molecule and has given the name tautomerism to this phenomenon. The mobility of liquids is therefore a result of tautomeric re-arrangements of the atoms.

Evaporation, condensation, freezing, melting, solution, adsorption, and surface tension, and even viscosity, are thus chemical phenomena, and chemical knowledge already available may be directly applied in their study.

This theory has been applied with marked success in the study of the adsorption of gases by solids. Adsorbed gases are regarded as being chemically combined (either primary or secondary valence) with the *atoms* forming the surface of the solid. The adsorbed film thus usually consists of a *single* layer of atoms or group molecules, which forms a continuation of the structure of the solid. The effect of such films on the catalytic activity of surfaces (as, for example, platinum) depends entirely upon the nature and the arrangement of the atoms forming the actual surface of the solid.

In a similar way a theory of surface tension is now proposed in which the structure of the *surface layer of atoms* is regarded as the principal factor in determining the surface tension (or rather surface energy) of liquids. This theory is supported in the most remarkable way by all available published data on the surface tension of organic liquids.

According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface layer. By "active portion" of a molecule is meant a portion which is characterized by a strong stray field (residual valence). Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum.

The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

In liquid hydrocarbons of the paraffin series, the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

form the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact, the surface energy of all these many different substances from hexaine to molten paraffin, have substantially the same surface energy — namely, 46 to 48 ergs per square centimeter, although the molecular weights differ very greatly.

If, now, we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies* are *practically identical with those of the hydrocarbons.* The reason for this is that the surface layer in both cases consists of CH_3 groups.

With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy.

Particularly interesting relations are found with benzol derivatives.

In benzol itself, the group molecules arrange themselves so that the benzol rings lie flat on the surface, since the flat sides of these rings are the less active portions of the molecules. The surface energy of benzol is about 65 ergs per square centimeter.

If, now, an active group, such as OH, is substituted for one of the hydrogens in the benzol (forming phenol or carbolic acid), this group is drawn into the body of the liquid, *tilting the benzol ring up on edge* and raising the surface energy to about 75 ergs per square centimeter, which corresponds to the activity of the perimeter of the benzol ring. Thus *any active group* strong enought to tilt the ring up on edge raises the surface energy to about 75. Two active groups side by side (ortho position) have no greater effect than one. But two active groups opposite one another (para position) cannot both go wholly below the surface, so that the surface energy then becomes abnormally large (about 85 in case of para nitrophenol). The substitution of methyl or ethyl groups in the benzol ring lowers the surface energy except where an active group in an adjacent position draws these groups below the surface.

Some of the best evidence in support of the new theory is derived from experiments on thin films of oil on water or mercury. Oleic acid on water forms a film one molecule deep, in which the hydrocarbon chains stand vertically on the water surface with the COOH groups in contact with the water.

Acetic acid is readily soluble in water because the COOH group has a strong secondary valence by which it combines with water. Oleic acid is not soluble because the affinity of the hydrocarbron chains for water is less than their affinity for each other. When oleic acid is placed on water the acid spreads upon the water becauses by so doing the *COOH can dissolve in the water* without separating the hydrocarbon chains from each other.

When the surface on which the acid spreads is sufficiently large, the double bond in the hydrocarbon chain is also drawn down on to the water surface, so that the area occupied is much greater than in the case of the saturated fatty acids.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Oils which do not contain active groups, as for example pure paraffin oil, do not spread upon the surface of water.

The measurement of the area of water or mercury which can be completely covered by a given amount of a substance affords an accurate method of determining the shapes of group molecules. Thus it is found that the molecules of stearic acid on a surface of water have a length of about 23×10^{-8} cm and cover an area of 24×10^{-16} sq. cm. These measurements prove that the molecules are not spherical but are much elongated.

This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.

The size of the colloidal particles is determined by the difference in size between the two ends of the molecules just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed.

In the final publication of this paper the bearing of the shapes of molecules on the formation of colloids will be discussed in detail.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE SHAPES OF GROUP MOLECULES FORMING THE SURFACES OF LIQUIDS

Proceedings of the National Academy of Sciences
Vol. III, 251, April (1917).

IN A RECENT paper[1] I have developed a theory according to which all the forces involved in the structure of solids and liquids, are similar in nature to the forces causing chemical combination. Thus condensation, evaporation, adsorption, cohesion, crystallization, liquefaction, viscosity, surface tension, etc., are manifestations of the forces already known to the chemist. In all these cases the range of the forces is limited to atomic dimensions except in so far as their effects may be transmitted from atom to atom. According to this theory, every atom in a solid or liquid is chemically combined to every adjacent atom. This chemical union may be strong or weak and may be characterized either by primary or secondary valence (Werner).

In most inorganic solid or liquid substances of the strongly polar type, the identity of the molecule is wholly lost, but in organic compounds the groups of atoms constituting the chemical molecule usually have a real existence even in the liquid or solid state. These group molecules are held together by primary valence forces while the forces acting between the group molecules, although no less chemical than the others, are to be characterized as secondary valence forces.

From this viewpoint the forces involved in adsorption and surface tension do not originate from the group molecule as a whole, but rather from certain atoms in the molecule.

This theory leads inevitably to the conclusion that adsorbed films on plane surfaces of solids or liquids should, in general, be one atom or group molecule in thickness. Considerable experimental evidence has already been presented that this is the case with films of gases adsorbed on solids.

Miss A. Pockels[2] showed, in 1891, that very small amounts of oil on the surface of water have no appreciable effect on the surface tension, but that the surface tension begins to *decrease suddenly* when the amount of oil per unit area is increased beyond a certain sharp limit.

---

[1] Langmuir, I., *J. Amer. Chem. Soc., Easton, Pa.* **38**, 1916, (2221).

[2] Pockels, A., *Nature, London* **43**, 1891, (437–439).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Lord Rayleigh[3], Devaux[4], and Marcelin[5] have made similar experiments and have concluded that the amount of oil needed to produce an appreciable effect on the surface tension corresponds to a layer one molecule deep. Devaux finds with triolein that a film 11×10^{-8} cm thick just begins to lower the surface tension of water. From the density and molecular weight of the oil and from Perrin's value of the Avogadro constant, he calculates that the diameter of the molecule would be 11.3×10^{-8} cm if this be assumed spherical in shape.

According to my theory, however, molecules should not be regarded as spheres, since such a supposition would not be consistent with the chemical nature of the forces. The fundamental question immediately arises: What causes the spreading of an oil upon the surface of water? If we regard molecules as spheres, any attraction between the water and the oil should cause the oil to dissolve in the water instead of spreading on the surface. From the chemical viewpoint, however, the force causing the spreading should be a force between atoms, not between molecules. Evidently, then, some atom or atoms in the oil must have an affinity for the water. Now it is known that the presence of the —COOH, —CO, or —OH groups in an organic molecule tends to render the substance soluble in water, while the hydrocarbon chain decreases the solubility. On the other hand, hydrocarbons are soluble in each other. Therefore the —COOH, —CO, and —OH groups have more affinity for water than for hydrocarbons, while hydrocarbons have more affinity for each other than for water.

Thus, when an oil is placed on water, the —COO— groups combine with the water, while the hydrocarbon chains remain combined (secondary valence of course) with each other. This process leads directly to the spreading of the oil on the surface. If only a limited amount of oil is placed on a large surface, the spreading ceases as soon as all the available —COO— groups have come into contact with the water, for any further spreading would separate the hydrocarbon chains from each other.

According to this conception, pure hydrocarbon oils would not spread on water. Experiment shows that this is actually the case[6].

The theory furthermore indicates that the hydrocarbon chains in the oils must be placed above the —COO— groups on the surface. Thus, in a series of homologous compounds, as the length of the chain increases the thickness of the oil film should increase in proportion, while the area occupied by each molecule should remain constant.

Now the area occupied by each molecule, which we will designate by a, is readily calculated. If w is the weight of oil placed on the surface and A is the area to which the film must be compressed before the surface tension changes, then the area a covered by each molecule is evidently $a = AM/wN$, where

---

[3] Lord Rayleigh, *Phil. Mag., London* **48**, 1899, (331–337).

[4] Devaux, W., *Washington, Smithsonian Inst., Ann. Rep.* 1913, (261–273).

[5] Marcelin, A., *Paris, Ann. Physique* **1**, 1914, (19–34).

[6] Hardy, W. B., *London, Proc. R. Soc.* (A) **86**, 1912, (610–635).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

M is the molecular weight of the oil (oxygen = 16), and N is the Avogadro constant (6.06×10^{23} molecules per gram molecule). Furthermore, we may calculate τ the length of the molecule (measured vertically), as follows: the volume of each molecule is $M/\varrho N$, where ϱ is the density of the oil. By dividing this volume by a, the cross-section of the molecule, we obtain the length of the molecule, thus $\tau = M/a\varrho N = W/\varrho A$.

To measure A, a new method has been developed. A strip of paper, floating on the water in a long tray, is fastened to a horizontal balance. Oil is placed on the water on one side of the strip only, and leakage of oil past the ends of the strip is prevented by localized blasts of air from two small tubes. Thus the force tending to cause spreading of the oil is measured for different values of A. By plotting these results it is easy to extrapolate to zero force and thus obtain the maximum area completely covered by the oil film.

TABLE I

Cross Sections and Lengths of Molecules

Substance	M	Cross section a	$\sqrt{a}$	Length τ
		sq. cm $\times 10^{-16}$	*cm* $\times 10^{-8}$	*cm* $\times 10^{-8}$
Palmitic acid $C_{15}H_{31}COOH$	256	24	4.9	19.6
Stearic acid $C_{17}H_{35}COOH$	284	24	4.9	21.8
Cerotic acid $C_{25}H_{51}COOH$	396	25	5.0	29.0
Cetyl alcohol $C_{16}H_{33}OH$	242	21	4.6	21.9
Myricyl alcohol $C_{30}H_{61}OH$	536	29	5.4	35.2
Tristearin $(C_{18}H_{35}O_2)_3H_5$	891	69	8.3	23.7
Cetyl palmitate $C_{15}H_{31}COOC_{16}H_{33}$	482	21	4.6	44.0
Oleic acid $C_{17}H_{33}COOH$	282	48	6.9	10.8
Triolein $(C_{18}H_{33}O_2)_3C_3H_5$	885	145	12.0	11.2
Trielaidin $(C_{18}H_{33}O_2)_3C_3H_5$	885	137	11.7	11.9
Ricinoleic acid $C_{17}H_{32}(OH)COOH$	297	90	9.5	5.8
Linoleic acid $C_{17}H_{31}COOH$	280	47	6.9	10.7
Linolenic acid $C_{17}H_{29}COOH$	278	66	8.1	7.6
Castor oil $(C_{17}H_{32}(OH)COO)_3C_3H_5$	929	280	16.8	5.7
Linseed oil $(C_{17}H_{31}COO)_3C_3H_5$	875	143	11.9	11.0

Table I gives the values of a and τ found for a number of different solid and liquid films on distilled water at 16°C. Palmitic, stearic, and cerotic acids all occupy the same area ($24. \times 10^{-16}$ sq. cm) per molecule. The length of the molecule in the vertical direction (τ) increases about in proportion to the number of carbon atoms in the chain. This is a direct proof that the molecules are oriented on the surface with the COOH groups in contact with the water, and the hydrocarbon groups placed vertically above them.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Dividing the value of τ by the number of carbon atoms in these molecules, we obtain an average of 1.19×10^{-8} cm. It is not likely that the carbon atoms in a hydrocarbon molecule are closer to each other than in a diamond, so that we must conclude that the carbon atoms in the chain are not arranged along a straight line, but in a zigzag fashion. The cross-section *a* is ample for such an arrangement.

The data for tristearin show that the three —COO— groups are all located on the surface of the water and that each occupies the same area as it does in the stearic acid molecule. The three chains are placed side by side. Cetyl palmitate occupies actually less space than palmitic acid. The two chains lie side by side, each having less than one-half the cross-section, but twice the length, that it has in palmitic acid or cetyl alcohol.

These results prove that the areas are determined by the space on the water required by the active groups —COO— or —OH and not by the cross-section of the hydrocarbon chain itself.

The unsaturated acids and esters occupy much larger areas than the saturated ones, and have correspondingly shorter lengths. This is clearly due to the double bond (and the —OH in ricinoleic acid) itself occupying a space on the water. Marcelin[5] has shown that when a globule of oleic acid is placed on a water surface, the film obtained is twice as thick as one which just alters the surface tension of water. Marcelin concludes that such a film is two molecules thick. The above data show that when the thin film of oleic acid is doubled in thickness, each molecule then occupies the same area as does one of stearic acid. Clearly, when an excess of oleic acid is added, the —COOH groups displace the double bonds and the chains assume an erect position on the surface.

These facts prove that the hydrocarbon chain is extremely flexible and has no definite shape of its own. The term "chain" thus describes its properties admirably.

The above method makes it possible to determine the lengths and cross-section of molecules of non-volatile, insoluble substances. Devaux has shown that oils spread on clean mercury surfaces as well as on water, so that it may be possible to study many substances soluble in water by this method.

For volatile or soluble substances, however, there is another method by which the cross-sections and lengths of molecules in the surfaces of liquids may be determined.

According to Gibbs' equation

$$q = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad (1)$$

we may calculate q the amount of material adsorbed per square centimeter in the surface of a liquid, by determining the rate at which the surface tension, γ, changes as the concentration of a dissolved substance, or that of a vapor

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

above the liquid, is altered. It has been pointed out by Milner[7] that when substances strongly depressing the surface tension are added to water, the surface tension varies linearly with the logarithm of the concentration for all except extremely dilute solutions. If we write equation (1) as follows:

$$q = -\frac{1}{RT}\frac{d\gamma}{d\ln c} \tag{2}$$

it is evident that under these conditions q is independent of the concentration. Milner thus calculates from Whatmough's data for acetic acid solutions, that q is 3.8×10^{-10} grams mol. per square centimeter over a rather wide range of concentrations. This should correspond to a monomolecular film. Multiplying the above result by N, we find that it corresponds to 23×10^{13} molecules per square centimeter. The area occupied by each molecule is the reciprocal of this, or 43×10^{-16} sq. cm per molecule. If the whole of this area were covered by a single molecule of acetic acid, the value of τ would be only 2.2×10^{-8} cm. It is therefore probable that the group molecule forming the surface layer contains water adsorbed around the acetic acid group. The polar character of the —COOH group should exert its influence on the CH_3 radical, causing it to pack into the surface layer surrounded by a definite number of water molecules. This hypothesis is in accord with the fact that acetic acid mixes in all proportions with water.

Still more conclusive evidence in support of the new theory is furnished by a paper by Szyszkowski,[8] in which surface tension data for water solutions of propionic, butyric, valeric, and caproic acids are given. The results are found to be given quite accurately by the purely empirical relation

$$1-\frac{\gamma}{\gamma_0} = b\log_{10}\frac{c+a}{a} \tag{3}$$

where γ is the surface tension of the solution and γ_0 is that of water; a and b are constants. Szyszkowski found that b had the same value, namely 0.411, for all the fatty acids investigated, while the constant a had a different value for each substance. Over a large part of the range of concentrations investigated, a was negligible compared to c so that the empirical equation 3 is equivalent to the relation found by Milner. That is, if we neglect a in (3) and differentiate, we obtain

$$\frac{d\gamma}{d\ln c} = -0.434\gamma_0 b\,. \tag{4}$$

Comparing this with (2),

$$q = \frac{0.434\gamma_0 b}{RT} \tag{5}$$

---

[7] Milner, S. R., *Phil. Mag., London* **13**, 1907, (96–110).

[8] Szyszkowski, B. v., *Zs. physik. Chem., Leipzig* **64**, 1908, (385–414).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

Since b was found to have the same value for all the fatty acids, this equation indicates that the same number of molecules of acid are adsorbed in the surface layer in each case. Placing $\gamma_0 = 73$ dynes per centimeter; $b = 0.411$, $R = 83.2 \times 10^6$ ergs per degree and $T = 290°K$ we find $q = 5.4 \times 10^{-10}$ gram mols per square centimeter. This corresponds to a value of a of 30.6×10^{-16} sq. cm per molecule. This agrees even better with our value of $24. \times 10^{-16}$ sq. cm per molecule for palmitic acid.

Donnon and Barker[9] have measured the amount of nonylic acid adsorbed in the surface of its water solutions and have compared the result with that calculated from surface tension measurements by Gibbs' equation. Both methods gave approximately the same results, averaging about 1.1×10^{-7} grams per square centimeter (independent of the concentration over a wide range). This corresponds to a value of a of 23.7×10^{-16} sq. cm per molecule, practically identical with the values for the fatty acids given in Table I.

We may therefore conclude that in moderately concentrated solutions of all substances which strongly depress the surface tension, the surface consists of a layer, *one molecule deep*, of the dissolved substance, and that there is never a transition layer in which the concentration varies progressively as we go further from the surface into the solution. The amount of solute required to form the monomolecular layer can be calculated from Gibbs' equation. The length and cross-sections of the molecules forming the surface layer may then be found.

In the case of solutions of inorganic salts, such as NaCl, the surface tension is greater than that of pure water and increases linearly with the concentration. Milner[7] pointed out, according to Gibbs' equation, that there is a deficiency of solute in the surface proportional to the concentration. Now this ls exactly what we should expect if the surface layer of these solutions consists of a single layer of group molecules of water. Milner shows that the deficiency of salt is 4.1×10^{-11} gram molecules of salt per square centimeter for a normal slution (c = 0.001). Hence we may place $q/c = -4.1 \times 10^{-8}$.

This result can be explained if we assume that there is a layer 4.1×10^{-8} cm thick on the surface which contains no salt. This then should represent the length of the water group mlolecule. It is interesting to note that practically this same value is obtained with solutions of all the different inorganic salts.

Taking the molecular weight of water in the surface to be 18, we find the cross-section of the water molecule to be 7.3×10^{-16} sq. cm.

It is believed that this method of studying the structure of liquid surfaces will prove to be of very general application. The writer is undertaking experiments to measure the cross-sections of molecules adsorbed on water surfaces from vapors. Thus, benzol vapor greatly lowers the surface tension of water, and in this way some knowledge may be obtained as to the shape of the

[9] Donnon, F. G., and Barker, J. T., *London, Proc. R. Soc.* (A) **85**, 1911, (557–573)

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

benzol molecules under different conditions. Of course other liquids than water may also be used.

There is a great deal of available data on surface tension of solutions in the literature which can serve this same purpose. I hope to refer to as many of these cases as possible, in a paper on the constitution of liquids which will soon be submitted for publication in the *Journal of the American Chemical Society*.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

THE MECHANISM OF THE SURFACE PHENOMENA OF FLOTATION

Transactions of the Faraday Society
Vol. XV, 62 (1920).

NOTWITHSTANDING the importance which the flotation process has assumed in the separation of ores, there has been comparatively little progress in the development of the underlying theory. It is recognized that the process depends on the formation of thin oil films on the particles of ore and that owing to the difficulty with which these particles are then wet by water they become readily attached to the air bubbles and are thus carried to the surface. As far as I know, however, no really satisfactory theory of these phenomena has been proposed. The remarkably selective action of some oils on certain ores and the effects produced by small amounts of acids and other substances are very imperfectly understood.

The object of this paper is not to offer a new theory of flotation, but rather to call attention to a theory of adsorption and surface tension which greatly aids in understanding these phenomena and which therefore should prove useful in developing any comprehensive theory of flotation. Some simple experiments will be described showing that the new viewpoint is applicable to flotation processes.

The surface phenomena of flotation may be divided roughly into three classes: the formation and properties of the froth; the oiling of the solid particles; and the adhesion of the oiled particles to the bubbles of the froth. The formation of the froth depends on the existence of a film of oil or other substance at the boundary between the air and water phases. The oiling of the solid particles involves the formation of a similar film at the surface of the solid. The adhesion of the particles to the bubbles depends primarily on the ease with which oily water wets the oily solid and this in turn is measured by the angle of contact between these oiled liquid and solid surfaces. The formation of the oil films on the surfaces of the water and the solid particles is a typical case of adsorption so that an understanding of the fundamental phenomena of flotation requires a knowledge of the nature of adsorption.

For several years I have been engaged in a study of high vacuum phenomena, especially the effects produced when various metals are heated in gases at very low pressures. In some cases the rate of disappearance (or clean-

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

up) of the gas was measured, while in others the electron emission from the heated metal was observed. In the course of this work it was frequently found that adsorbed films of extraordinary stability were formed on the surface of the metal. The evidence from a large number of such experiments indicated clearly that these stable films consisted of a single layer of atoms chemically combined to the underlying atoms of the solid. The adsorbed atoms were chemically saturated but the atoms in the surface of the metal were not saturated by their combination with the adsorbed atoms and therefore remained firmly held by the next underlying layer of metal atoms. This viewpoint was based to a large extent on the work of the Braggs on crystal structure.

The atoms in the very stable films referred to are clearly held to the surface by direct chemical union of the primary valence type, like that holding oxygen to carbon in carbon dioxide. Further investigation showed that in some other cases of adsorption such as that of nitrogen or argon by charcoal, etc., the forces involved, although no less chemical than the others, were of the type represented by secondary valence such as that holding water of crystallization, or ammonia in complex ammonia derivatives.

A further extension of this theory led to the view that no fundamental distinctions should be drawn between the so-called physical phenomena and those recognized as chemical. Thus condensation of vapours, crystallization, surface tension, adsorption, etc., are manifestations of forces of the same kind as those involved in the formation of chemical compounds.[1]

From this viewpoint, the forces involved in the adsorption of organic substances with large molecules do not originate from the molecule as a whole, but rather from certain atoms in the molecule. The theory indicates that adsorbed films in general should be one molecule in thickness. Lord Rayleigh in 1899 (*Phil. Mag.* **48**, 331 (1899)) observed that a film of olive oil just thick enough to lower appreciably the surface tension of water had a thickness of 1.0×10^{-7} cm. He stated: "Now this is only a moderate multiple of the supposed diameter of a gaseous molecule, and perhaps scarcely exceeds at all the diameter to be attributed to a molecule of oil. It is obvious, therefore, that the present phenomena lie entirely outside the scope of a theory such as Laplace's, in which matter is regarded as continous and that an explanation requires a direct consideration of molecules."

"If we begin by supposing the number of molecules of oil upon a water surface to be small enough, not only will every molecule be able to approach

---

[1] The evidence for these conclusions is given in the following papers by the writer: Chemical Reactions at Low Pressures. *J. Am. Chem. Soc.* **37**, 1139 (1915); The Constitution and Fundamental Properties of Solids, *J. Am. Chem. Soc.* **38**, 2221 (1916); and the Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum, *J. Am. Chem. Soc.* **40**, 1361 (1918). A review of this work is given by Wm. C. McC. Lewis in this recent *System of Physical Chemistry*, Longmans, Green and Co., 1918, Volume 1, pages 461–474.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the water as closely as it desires, but any repulsion between molecules will have exhausted itself. Under these conditions there is nothing to oppose the contraction of the surface — the tension is the same as that of pure water."

If the molecules "behave like smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely packed. According to this view the tension would remain constant up to the point where a double layer commences to form. The actual course of the curve of tension deviates somewhat widely from the above description, but perhaps not more than could be explained by heterogeneity of the oil whereby some molecules would mount more easily than others, or by reference to the molecular-motions which cannot be entirely ignored. If we accept this view as substantially true we conclude that the first drop in tension corresponds to a complete layer one molecule thick, and that the diameter of the molecule of oil is about 1.0×10^{-7} cm."

By a similar method Devaux (Ann. Report Smithsonian Inst. Washington (1913) 261) concludes that the diameter of the molecule of triolein is 11.3×10^{-8} cm if the molecule be assumed spherical in shape.

According to the present theory, however, molecules should not be regarded as spheres since such a supposition is not consistent with the chemical nature of the forces. The spreading of an oil on the surface of water is therefore due to an attraction between the water and some active group in the oil molecule. If the molecule as a whole had an affinity for water it would render it soluble in water. It is known that the presence of —COOH, =CO or —OH groups in an organic molecule increases the solubility in water while the hydrocarbon chain decreases it. On the other hand, hydrocarbons are soluble in each other. When an oil containing the carboxyl group is placed on water these active groups combine with the water, while the hydrocarbon chains remain combined with each other by secondary valence forces. On an unlimited surface the oil thus spreads until all the —COO— groups have come into contact with the water, forming a monomolecular film. A pure paraffin oil, since it contains no active groups, does not spread on water.

By measuring the greatest area of water that can be completely covered by a small weighed amount of oil it is possible to determine the cross sections and lengths of the molecules. The thickness of the oil film gives the length of the molecule measured vertically while the area covered by each molecule gives its cross section. Results obtained this way show that the molecules in oil films are not even approximately spherical. This is shown by the data of Table I.

Thus the molecules of the fatty acids from palmitic to cerotic are all of the same cross section, but their length increases in proportion to the length of the hydrocarbon chain. Tristearine has a cross section three times that of stearic acid, but the length of the molecule is the same. The areas covered

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

by the oils or fats are thus proportional to the number of active groups present. The molecule of cetyl palmitate is nearly ten times as long as it is wide ($\sqrt{a}$), while the molecule of triricinolein (castor oil) has a length only about one third of its width. The results show that these differences of

TABLE I

Cross Section a, and Length t of Molecules

Substance	Cross Section a sq. cm	$\sqrt{a}$ cm	Length t cm
Palmitic acid $C_{15}H_{31}COOH$	22×10^{-16}	4.7×10^{-8}	21.4×10^{-8}
Stearic acid $C_{17}H_{35}COOH$	22	4.7	23.8
Arachidic acid $C_{19}H_{39}COOH$ . . .	22	4.7	25.9
Cerotic acid $C_{25}H_{51}COOH$	22	4.7	33.0
Cetyl alcohol $C_{16}H_{33}OH$	21	4.6	21.9
Tristearine $(C_{18}H_{35}O_2)_3C_3H_5$	69	8.3	23.7
Cetyl palmitate $C_{15}H_{31}COOC_{16}H_{33}$.	21	4.6	44.0
Oleic acid $C_{17}H_{33}COOH$	48	6.9	10.8
Erucic acid $C_{21}H_{41}COOH$	44	6.6	14.2
Triolein $(C_{18}H_{33}O_2)_3C_3H_5$	145	12.0	11.2
Linoleic acid $C_{17}H_{31}COOH$	47	6.9	10.7
Linolenic acid $C_{17}H_{29}COOH$	70	8.4	7.1
Ricinoleic acid $C_{17}H_{32}(OH)COOH$ . .	100	10.0	5.2
Castor oil $[C_{17}H_{32}(OH)COO]_3C_3H_5$ . .	290	17.0	5.5

shape are strictly in accordance with the theory of the chemical nature of the phenomena.[1]

The same theory has been applied to surface tension phenomena in general. According to this theory the molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface. Surface tension is a measure of the potential energy of the stray field extending out from the surface layer of atoms. The molecules in the surface layer arrange themselves so that this potential energy is a minimum. The surface energy of a liquid is thus not a property of the molecule as a whole, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

In liquid hydrocarbons of the paraffin series the methyl groups at the ends of the hydrocarbon chains from the surface layer. The surface is thus

[1] The experimental and theoretical work underlying the above statements has been published in the following papers by the writer: Surface Tension Phenomena, *Met. Chem. Eng.* **15**, 468 (1916); The Shapes of Group Molecules forming the Surfaces of Liquids, *Proc. Natl. Acad. Scien.* **3**, 251 (1917); The Constitution and Fundamental Properties of Liquids, *J. Am. Chem. Soc.* **39**, 1848 (1917). A short summary of some of this work has been given by Wm. C. McC. Lewis, *Physical Chemistry*, Vol. 1, p. 474.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the same no matter how long the chain may be. As a matter of fact, the surface energy[1] of all the hydrocarbons from hexane to molten paraffin is substantially constant, namely 46 to 50 ergs per sq. cm, although the molecular weights differ very greatly.

If now we consider the alcohols CH_3OH, C_2H_5OH, etc., we find that their surface energies are practically identical with those of the hydrocarbons. The reason is that the surface layer in both cases consists of CH_3 groups. With such substances as CH_3NO_2, CH_3I the surface energy is much greater than that of the hydrocarbons. This is partly due to the fact that the large volume of the NO_2 or I forces the CH_3 groups apart and increases the surface energy. This theory was tested by the writer for a large number of organic substances for which data was available. Particularly strong support for the theory was found in the case of benzene derivatives. A few months after the publication of the writer's preliminary results, W. D. Harkins, who had independently arrived at somewhat similar views, published two papers[2] dealing in great detail with the surface tension at the interface of two liquids and with surface tensions of pure liquids. The data prove conclusively the general validity of the theory given, which is practically identical with that previously advanced by the writer.

In his first paper Harkins gives the values of the change of free surface energy when one sq. cm of interface is formed between two liquids. A few of these data are shown in Table II in the column headed $(-\Delta\sigma)$. In every case one of the two liquids forming the interface is water.

TABLE II

Change of Free Energy in Formation of an Interface with Water

Liquid	Temp.	$-\Delta\sigma$	σ	σ_0
Water (against water)	20°	145.6	72.8	110.0
Hexane C_6H_{14}	25°	41.2	18.7	49.5
Octane C_8H_{18}	20°	46.0	21.8	48.4
Paraffin oil	17°	47.8	31.8	54.2
Octylane C_8H_{16}	17°	72.9	22.3	—
Octyl alcohol $C_8H_{17}OH$	20°	91.8	27.5	50.8
Ethyl ether $(C_2H_5)_2O$	20°	79.2	17.1	48.4
Capryllic acid $C_7H_{15}COOH$	18°	93.7	28.8	—
Oleic acid	20°	89.0	32.3	—
Ricinoleic acid	16°	94.9	35.8	—
Ethyl nonylate	20°	77.0	28.0	—
Castor oil	17°	87.7	37.1	—
Benzene	20°	66.2	29.0	70
Benzyl alcohol	22°	107.4	39.7	39.7

[1] The total surface energy σ_0 is related to the surface tension σ by the equation $\sigma_0 = \sigma - T(d\sigma/dT)$ where T is the absolute temperature.

[2] W. D. Harkins, *J. Am. Chem. Soc.* **39**, 354, 541 (1917).

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

In the column headed γ is the free surface energy of the nonaqueous liquid against air, while the last column, γ_0, gives the total surface energy $\gamma - T(d\gamma/dT)$. It is readily seen both from this data and from theoretical considerations that $-\Delta\gamma$ is a measure of the activity of the *most active portion* of the molecule, while γ_0 is a measure of the activity of the *least active* part of the molecule. Thus in the surface of a substance like octyl alcohol the hydroxyl groups are drawn in towards the interior of the liquid and thus contribute little towards the surface energy γ_0. But when octyl alcohol is placed in contact with water the molecules forming the interface are oriented so that the hydroxyl groups come in contact with the water. The free surface energv γ is only very approximately a measure of the strength of the least active portion of the molecule. The size of the molecule determines the amount of thermal agitation and influences the value of γ, whereas γ_0 is usually independent of temperature and depends only slightly on the size of the molecule.

It is apparent that considerations of this kind must be of fundamental importance in connection with the theory of the flotation process. Before much progress in this direction can be made, however, it is necessary to develop experimental methods for the investigation of oil films on solid bodies. With this end in view I have undertaken some simple experiments along these lines.

Experimental Part

A study was first made of properties of cleaned and oiled glass surfaces. It was especially desired to find how much oil must be present on a glass surface to alter materially its properties.

Microscope slides were washed with soap and water, were heated in a mixture of concentrated sulphuric acid and chromic oxide, and were finally washed in running tap water and dried over a Bunsen burner flame. During this whole treatment they were held in a pair of forceps. This method of cleaning proved to be much more thorough than any other method tried.

When a drop of clean water is placed on a slide cleaned in this way the water wets the glass readily, and when the slide is inclined the surplus water runs to one end, leaving a thin film of water over the whole surface of the glass. Another indication of the cleanliness of the surface is obtained by dipping the slide into a clean surface of water on to which a small amount of talc powder has been dusted. The talc particles are not repelled from the glass surface if it is clean, but very small amounts of grease can be detected by the motion of the talc particles produced by the spreading of an oil film on the surface of the water. This test for the cleanliness of a surface will be referred to as the talc test.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Another characteristic of a thoroughly cleaned glass surface is the extraordinary friction observed when the glass is rubbed with another clean piece of glass or platinum. Lord Rayleigh[1] has recently called attention to this fact and pointed out its significance in connection with the theory of lubrication. It is also interesting to note that Faraday in his Experimental Researches (paragraph 369) mentions the "peculiar friction" observed when a platinum rod was rubbed over a surface of a platinum plate which had been thoroughly cleaned by making it cathode in electrolysis or by heating it in concentrated sulphuric acid.

In order to study this effect quantitatively some small glass sliders ranging from 0.2 to 1.0 gram in weight were made by bending glass rods in the form of a horseshoe and well rounding the ends. The two arms of the horseshoe were then arched in a plane perpendicular to the original plane of the horseshoe so that when the slider was laid on a flat surface it touched in three definite points. If one of these sliders was placed on a clean slide it was found that the slide could be tilted usually to an angle of 70° from the horizontal, often 75°, and in some cases 90° or even 92° before it would begin to slide. Of course, before beginning this test it is essential to celan the slider by the method already given. If the slider was forced over the surface of the slide a squeaking noise was always heard if the glass was clean and the surface of the glass was scratched perceptibly in the process. It was found that much more consistent results were obtained if when the glass was tilted the slider was pushed over the surface by means of a pair of forceps. The angle was measured at which the slider would just stop moving after being set in motion by the forceps. The sliding angle thus found varied between 50° and 60° for different samples of glass cleaned by the method described. On standing in the air for a short time the surface becomes slightly contaminated, so that the sliding angle decreases. Thus after three minutes the angle is 45°, after 20 minutes 40°, after two hours 22°. This contamination is also shown by the talc test. The actual size of the slider used seemed to be without effect on the results.

If a small amount of oleic acid or other oily substance is placed upon a clean glass slide and this is then throughly wiped with a clean cloth, it is found that the sliding angle decreases to a value ranging from about 6° to 10°. The talc test can be tried repeatedly with such a surface and each time the slide is moved up or down in the water a fresh contaminated area is produced. By holding an oiled slide under running water in such a way that the water continually advances and recedes from the oily surface the surpuls oil may ultimately be removed so that no contamination is indicated by this talc test. The sliding angle, however, remains small. The friction test is thus much more sensitive than the talc test.

---

[1] *Phil. Mag.* **35**, 157 (1918).

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

If pure paraffin oil is placed on a clean slide the oil readily wets the glass very much as water does, whereas oleic acid draws together on the glass in globules. The paraffin oil lowers the sliding angle nearly as effectively as oleic acid, but the behaviour of such a surface towards water is radically different. Thus if a clean slide covered with paraffin oil be held under a very gentle stream of water the paraffin detaches itself from the glass in large drops and the glass becomes wet by the water. If the slide is then dried at low temperature it is found that the sliding angle is 40° or more, showing that all paraffin oil has been removed from the glass.

In order to put a monomolecular film of oil on a glass surface the following method was adopted. The surface of water in a long narrow tray was cleaned by scraping with a strip of paper extending across the tray. A very small quantity of oleic acid was placed on the water at one end of the tray and the spreading of the film was made visible by traces of talc powder. By adding the oil in very small portions the surface was finally saturated with oil without leaving any globules of oleic acid except at the end of the tray at which they had been added. Previous work had shown that an oleic acid film formed in this way has a thickness of 22×10^{-8} cm and consists of a single layer of molecules each occupying an area of about 24×10^{-16} sq. cm, the spacing thus being the same as that of stearic acid and the other saturated fatty acids. The cleaned slide was then dipped edgewise into the water covered by this film and slowly withdrawn. As the slide was raised it remained at first wetted by the water and the film of oil spread itself over the newly formed water surface. The motion of small particles of talc showed that the oil film moved upward at the same rate as the slide was raised, so that there was no concentration of oil on to the surface of the glass. When a clean slide is originally dipped into the water the talc particles close to the surface do not move either towards or away from the slide. This indicates that no oil goes on to the glass surface while this is being lowered into the water. This remarkable fact is confirmed by removing the oil film from the surface of the water by scraping and blowing before withdrawing the slide from the water. If the slide is then dried at ordinary temperature it is found both by the talc test and the friction test that the surface is still entirely free from oil. If on the other hand the slide has been raised from the surface saturated with oil and is held in a vertical position the water film gradually moves down and the oil film on it comes into contact with the glass. The same result may also be obtained by holding the slide in a horizontal position and allowing the water to evaporate. In this way the glass surface is covered with a film of oil of the same thickness as that originally present on the surface of the water.

A slide treated in this way appears just as clean as before, but if dipped in clean water it is found that the water no longer adheres to it but gradually runs off, as from a greasy surface. The talc test gives a rather slight indica-

Digitized by Google Original from UNIVERSITY OF MICHIGAN

tion of contamination, but if the slide is raised and lowered repeatedly in pure water, or is passed several times through a gentle stream of running water, it soon loses its ability to contaminate water. The friction test gives a sliding angle of about 6° to 10°, whether or not the surface has been washed by clean water before drying.

In other experiments the film of oleic acid was allowed to expand on the water surface until the surface tension was nearly that of pure water. The thickness of such a film (*see* Table I) is 11×10^{-8} cm, and the area covered per molecule is 48×10^{-16} sq. cm. A glass slide oiled by dipping and slowly withdrawing from this oiled water and drying in a horizontal position gave sliding angles ranging from 6° to 20°. The results were rather erratic and indicated that the oil was not uniformly distributed over the slide, but was concentrated somewhat on those portions which were the last to dry. If the slide was allowed to dry in a vertical position, the upper part of the slide was found entirely free from oil, while the rest of the slide was uniformly covered.

Mica.—Freshly split mica (biotite) is very readily wetted by water and by paraffin oil, but oleic acid and molten stearic acid form globules. These acids, however, leave the surface greasy even after the globules have been removed. Paraffin oil behaves as it does on glass, that is, a gentle stream of water displaces it completely from the surface. Dipping the clean mica into a water surface saturated with oleic acid does not contaminate the mica, but withdrawing it and allowing the water to evaporate gives an oiled surface. This differs, however, markedly from an oiled surface of glass. The oil is given up in larger quantity in the talc test, and after the surface has been repeatedly passed through a stream of water, it becomes wetted nearly as easily as a surface of freshly split mica.

A glass or platinum slider gives a sliding angle of about 10° on clean mica and about 6° on mica which has been dipped in water and saturated with oleic acid. The slipperiness of clean mica as compared with clean glass (sliding angle 60°) is very striking.

Platinum.—A smooth piece of platinum foil (1½ by 3 inches) was polished with sea sand and ignited to a red heat. It was readily wet by water. As in the case of glass and mica, platinum does not become contaminated when dipped into oiled water, but only when it is drawn out and dried. Clean platinum gives a sliding angle of 35° with a platinum slider, and 30° with a glass slider. After dipping once in water saturated with oleic acid and drying, the sliding angle with both glass and platinum sliders was 14°. By a second dipping the angle fell to 6° with the glass and 12° with the platinum slider. The surface after single dipping loses very little, but after double dipping loses a considerable quantity of oil in the talc test. The loss of this oil does not increase the sliding angle. It seems that only the oil which is not in true contact with the platinum is lost during the talc test. Repeated passing through a stream of water does

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

not increase the sliding angle or the tendency of water to gather into globules on the oiled platinum surface.

Paraffin oil behaved the same on platinum surfaces as on those of glass.

Calcite, sphalerite, galena, pyrites, and magnetite.—Fresh cleavage surfaces or fractures of these minerals were all readily wetted by water or paraffin oil, and in each case the paraffin oil was readily displaceable by water. The clean surfaces all became greasy by dipping into water saturated by oleic acid, and in every case it was impossible to remove the greasiness by repeatedly passing through a stream of water. On cleavage surfaces of calcite and galena rough qualitative observations showed that there was a peculiar friction, as in the case of glass.

Measurement of Contact Angles of Drops of Water on Oiled Surfaces

Simple observation showed that drops of water behaved rather differently on various solid surfaces which had been dipped into water saturated by oleic acid.

Drops of water placed on oiled glass flattened out to a layer about 2 mm thick. By tilting the glass the drop would advance over the surface at the lower edge, forming a rather large angle of contact, while at the rear edge the water would recede from the glass rather slowly, and the angle of contact was much less than at the advancing edge. The moving drop was usually rather irregular in outline. On mica the depth of the drop is less than on glass, and the drops are more irregular in shape after moving over the surface. With platinum the drops of water become thicker and more symmetrical in shape, while on galena they show a still greater thickness and regularity.

To obtain more definite information, drops of water ranging from 0.7 to about 1.22 cc. in volume were placed on oiled surfaces and their heights measured by a vernier attached to a fine point brought into contact with the drop and subsequently with the solid surface on which the drop had rested. The results are given in Table III. The figures in the columns marked h represent the depths of the drops in millimeters, while θ is the average contact angle as calculated from the equation

$$h = a\sqrt{2}\sin\left(\frac{1}{2}\theta\right) \tag{1}$$

where a is given by

$$a = \sqrt{2\,\delta/(g\varrho)} \tag{2}$$

Here δ is the surface tension; g the acceleration of gravity, and ϱ the density of water. This equation is accurate only for large drops. Those actually used ranged from 1.4 to 2.5 cm in diameter, and a further increase in the size of the drop did not appreciably alter the value of h.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

In each case the oily surface was prepared by dipping a thoroughly cleaned (or cleavage) surface into water saturated with oleic acid, and drying at low temperature. The water drop was then placed on the surface and this was shaken and sometimes tilted slightly, so that the drop reached a stable shape. The results given are the averages of several observations. In most cases the individual observations on different drops agreed within about 0.1 mm in the value of h.

The measurements of the column marked I were made with drops of clean water. In many cases the drops were slightly contaminated by oil from the solid surface. In every case a very small amount of talc was dusted on to the

TABLE III

Height and Contact Angles of Water Drops on Surfaces Covered by Monomolecular Films of Oleic Acid

Solid	I Clean water		II Water saturated with oleic acid	
	h	θ	h	θ
	mm			
Mica	0.9	18°	0.9	24°
Quartz	—	—	1.2±	31°±
Glass	2.1	45°	1.5	42°
Platinum	2.9	65°	2.45	72°
Calcite	3.1	70°	2.75	82°
Sphalerite	3.6	82°	3.0	92°
Galena	3.7	86°	3.35	106°

drop after measuring it, and by gently blowing on it the contaminated surface was forced to one side where its area could be estimated. The areas were always less than about 60 or 70 per cent of the whole surface, so that the surface tension of the drop could not have been appreciably affected. This conclusion was checked in some cases by repeating the measurements after the surface had been washed by passing through a stream of running water until drops placed on the surface were no longer contaminated. In each case (except mica) the results remained unaltered. In calculating the angles of contact, γ in the above equation (2) was placed equal to 72.8, so that equation (1) became

$$h = 0.546 \sin\left(\frac{1}{2}\theta\right). \qquad (3)$$

The measurements given in column II of Table III were made after the drops of water had been touched by a wire dipped in oleic acid. In this case γ of equation (2) was taken to be 42.8, so that the coefficient of Equation (3) was 0.418 instead of 0.546.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

A few measurements of water drops were made on surfaces of paraffin. stearic acid, cetyl alcohol, myricyl alcohol and cetyl-palmitate (spermaceti), These were prepared by spreading the molten fat or wax over a glass slide while cooling. All these substances except paraffin tend to draw up into globules on the glass; cetyl alcohol does this particularly strongly. To get a uniform coating it was necessary to "iron out" the wax by a heated glass rod.

On solid paraffin the height (h) of the drop was 4.4 mm (2.5 mm after adding oleic acid). The contact angle of the pure water was thus 110°. The drop in this case tends to slide over the glass with the utmost ease — a drop weighing 0.8 gram slides when the inclination of the surface is only about 2°.

With stearic acid h was 3.9 mm, but this could only be realised after prolonged washing of the surface to prevent contamination of the drop. The drops of water are much less mobile than on paraffin, thus a drop of 0.8 g does not slide over the surface until the inclication is 6° to 8°.

Myricyl alcohol gave $h = 4.1$ and gave results resembling those on paraffin. Cetyl palmitate also resembled paraffin. Cetyl alcohol on the other hand became wetted (or nearly so) by the water, but the water had become completely covered by a film. Even very prolonged washing of the cetyl alcohol did not prevent this contamination of the surface of water drops. These results are cited only to show how remarkably specific the properties of these various substances are.

Discussion of Experimental Results

The experiments have shown clearly that oil films of molecular thickness are sufficient to alter radically the surfaces of solids. This is shown not only by the lubricating properties of these films but also by the contact angles made by water drops.

The properties of these monomolecular films as measured by their contact angles depends apparently as much on the character of the underlying solid as upon the nature of the oil. Thus the minerals galena and sphalerite give much larger contact angles when contaminated by oleic acid than those obtained with glass or quartz under similar conditions. This result seems to be inconsistent with the theory of surface tension discussed in the early part of this paper according to which the surface tension depends only on the nature of and arrangement of the atoms forming the actual surface. From this viewpoint we would be led to believe that the upper surface of oil films on solid bodies should in every case consist of CH_2 or CH_3 groups, and thus the properties of all the films should be similar. However, there in an important distinction between the case of an oil film covered by a water drop and the surface layer of a pure organic liquid. The water drop on the film tends to draw the active groups to itself. In the case of oleic acid there are two active groups in the molecule, namely, the carboxyl and the double bond. It is probable that in some cases both of these are rather firmly held by the underlying solid, while in

Digitized by Google Original from UNIVERSITY OF MICHIGAN

others only the carboxyl group is so held and the double bond is free to come in contact with water. Thus on galena we may assume that both active groups are held by the solid so that the water has only a little more tendency to spread on the oiled surface than on solid paraffin. With glass, on the other hand, some of the active groups may be brought to the upper surface by contact with water so that the water spreads, much more easily than over paraffin. This theory readily explains the marked difference between the contact angle of an advancing and receding surface on glass contaminated by oleic acid.

Another factor which must be taken into account is that the spacing of the molecules in oil films on solids must be determined primarily by the surface lattice of the solid, whereas with films on liquids the molecules are able to arrange themselves largely without reference to the underlying liquid. As a result the films on solids are ordinarily not in stable equilibrium; many molecules are crowded into spaces too small for them, while others may occupy unnecessarily large areas. As a matter of fact in all the experimental work with films on the solids the results were much more irregular and depended much more on slight differences in the previous history of the film than was the case with films on liquids.

To test this theory more fully it will be desirable to repeat experiments of the type described above with many different kinds of oils and fatty substances.

The explanation of the ease with which paraffin oil wets solid surfaces and yet is easily displaced by water is probably as follows: We may assume that the attractive force between hydrocarbon molecules and the solid surface is greater than that between hydrocarbon molecules, but active groups like those contained in water or oleic acid are attracted to the solid surface very much more than are hydrocarbon molecules. The paraffin oil thus readily wets the solid if brought into contact with it, but the hydrocarbon molecules are readily displaced from the surface layer when either water or oleic acid is present. When oleic acid is forced over the surface of glass a monomolecular layer of this substance covers the glass. The acid draws into globules on this surface, however, because by so doing the active groups can come into contact with each other (probably forming clusters), whereas if they remained spread out on the surface they could only come into contact with the less active portions of the molecules forming the surface film. It is evident that this tendency to gather into globules does not occur with pure paraffin oil.

The fact that clean solid surfaces do not become contaminated when dipped into a water surface saturated with oleic acid is readily explained by the fact that the active groups of the surface film are in contact with the water and are thus turned away from the solid surface while this is being pushed down into the water. On drawing it out, however, the active groups of the surface film are on the side nearest to the solid surface.

The peculiar property of mica in giving such a small sliding angle even when cleaned indicates that the surface is covered with water molecules with

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

their hydrogen atoms thoroughly saturated and turned outwards to form the surface layer. The great ease with which mica cleaves and the readiness with which oil films can be washed off and water can spread on these oil films is also a result of the small residual field of force extending out from these surface hydrogen atoms.

Application to the Theory of Flotation

Formation of Froth.—The formation of froth depends on the presence of substances which can form a stable monomolecular film over the surface of each bubble. In order that froth may readily form it seems to be desirable to have present a soluble substance having a strong tendency to be adsorbed on the surface of the liquid. For example, a small amount of acetic acid added to water produces a rather unstable froth. As we go to the higher fatty acids, for example valeric acid, the tendency to form a froth is much increased. On the other hand, oleic acid does not readily produce a froth unless it is rendered soluble in water, as for example, by forming soap by the addition of sodium hydroxide. Oil of pine tar, so often used as a frothing agent, contains soluble substances that probably act in this way. The presence of alkalies in flotation is to be avoided probably because the hydroxyl ion tends to draw the carboxyl group of the fatty acid to itself rather than to allow it to attach itself to the solid particles.

Oiling of the Solid.—The particular properties of different kinds of oils for this purpose must be made the subject of further careful study. The presence of small amounts of acid and substances which become adsorbed on the solid surfaces or attach themselves to the oil films would be expected to alter the results materially. This subject is, of course, a very large one, and will necessitate much experimental work before it becomes well understood.

Constant Angle of Solid Particles.—The tendency of the particles to attach themselves to the bubbles of the froth is measured by the contact angle formed between the oily surface of the bubble and the contaminated surface of the solid. For the case where oleic acid forms both films the data given in column II of Table III are applicable. The results indicate that the selective action by which substances like galena are separated from quartz and calcite is dependent upon the contact angle formed by the oiled surfaces rather than by any selective tendency for the oil to be taken up by some minerals more than by others.

The object of this paper has been to show the applicability of a rather new viewpoint and particularly to stimulate further research into the mechanism of the flotation proces. The writer is much indebted to Miss Katharine Blodgett for carrying out most of the experimental work.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

SURFACE CHEMISTRY[1]

NOBEL LECTURE, PRESENTED IN STOCKHOLM ON DECEMBER 14, 1932

THE PHENOMENON of adsorption has been known and has been studied for many years. For example, Sir James Dewar found that charcoal cooled in liquid air was capable of taking up large quantities of such gases as oxygen and nitrogen. This was known to be a surface action depending on the very fine state of division of the charcoal.

The effect of soap in lowering the surface tension of water depends upon the presence of a higher concentration of soap molecules in the surface layer than in the solution.

Willard Gibes proved thermodynamically that there is a general relation between the surface adsorption, the lowering of the surface tension and the concentration of the solution. The equation that he deduced can readily be put in the form

$$\frac{dF}{d(\ln p)} = \sigma kT, \tag{1}$$

where p is the partial pressure of the vapor of the adsorbed substance in equilibrium with the surface of the liquid, or it may be the partial osmotic pressure of a substance dissolved in the liquid, σ is the number of molecules adsorbed on the surface per unit area, T is the absolute temperature and k is the Boltzmann constant 1.37×10^{-16} erg deg^{-1}, and F, which may be called the spreading force, is given by

$$F = \gamma_0 - \gamma, \tag{2}$$

where γ_0 is the surface tension of the pure solvent (in dynes cm^{-1}) and γ is the surface tension of the solution.

The form of Gibbs' equation represented by Eq. (1) is thermodynamically valid if the film is in equilibrium with the 2 volume phases and if the law of ideal gases

$$p = nkT \tag{3}$$

is applicable in the volume phases.

---

[1] This paper is designed to summarize the author's contributions and present views in this field, but does not adequately describe the work of others.

[EDITOR'S NOTE: This paper also printed in *Angewannte Chemie* **46**, 719 (1933); also printed in *Chem. Rev.* **13**, 147 (1933). It also appears as Chapter Four in the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Prior to 1910 many different theories of adsorption had been proposed, but none of them had been very successful. In most of these theories the increased concentration of the adsorbed substance near the surface was thought to be analogous to the retention of the earth's atmosphere by the gravitational attraction of the earth. An adsorbed gas was thus regarded as a kind of miniature atmosphere extending out a short distance from a solid substance. In general such theories were called upon to account only for qualitative aspects of the adsorption of gases on solids. Most of the knowledge of adsorption was empirical. Even Gibbs' law had not been verified experimentally.

When I first began to work in 1909 in an industrial research laboratory (1) (2), I found that the high vacuum technique which had been developed in incandescent lamp factories, especially after the introduction of the tungsten filament lamp, was far more advanced than that which had been used in university laboratories. This new technique seemed to open up wonderful opportunities for the study of chemical reactions on surfaces and of the physical properties of surfaces under well defined conditions. I resolved to try the effect of introducing very small quantities of various gases into a highly evacuated bulb containing a tungsten filament. Since by a McLeod gauge pressures as low as 10^{-8} atmospheres could be measured, it was possible to observe the disappearance of an amount of gas of less than 0.1 cubic millimeter measured at atmospheric pressure. The use of a tungsten filament presented particular advantages for this could be heated in high vacuum to temperatures of over 3000°K, so that all impurities could readily be distilled out of the filament. The ease and accuracy with which any desired temperature could be produced and measured was also important.

When a hot body, such as a filament, is in contact with a gas at atmospheric pressure in a glass bulb, the convection currents and the uncertain temperature distribution in the gas are factors which greatly complicate any interpretation of observed phenomena involving the interaction of the filament with the gas.

If the gas, however, is at a pressure as low as 100 baryes[1], the mean free path of the molecules is many times greater than the diameter of the ordinary tungsten filament. Each molecule which strikes the filament has thus made so many collisions with the bulb since its last collision with the filament, that the effective temperature of the gas in contact with the filament may be taken to be the same as that of the bulb. The disturbing effects of convection currents are then entirely eliminated and the rate of arrival of gas molecules at the surface of the filament can be calculated according to the laws of the kinetic theory of gases. This theory leads to the equation

$$\mu = \frac{p}{(2\pi mkT)^{1/2}}, \qquad (4)$$

[1] A barye or c.g.s. unit of pressure, 1 dyne cm^{-2}, is almost exactly 10^{-6} atmospheres.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

where μ is the rate of arrival of the gas molecules expressed in molecules cm^{-2} sec^{-1}, and m is the mass of the molecule. By inserting numerical values this equation becomes

$$\mu = 2.65 \times 10^{19} p (MT)^{-1/2}, \qquad (5)$$

where M is the molecular weight of the gas (oxygen = 16) and p is expressed in baryes. By using filaments of small size and bulbs of large size, it was possible to measure experimentally such high rates of disappearance of gas (clean-up) that every molecule that struck the filament disappeared. Under usual conditions, however, the rates of clean-up were far less than this theoretical maximum. The fraction, ε, of all the impinging molecules which reacted on striking the filament could thus be determined.

Working in this way, a systematic study was undertaken of the effects of such gases as oxygen, hydrogen, nitrogen, carbon monoxide, and their mixtures, etc., on filaments of tungsten, carbon, molybdenum and platinum. I shall refer only to those cases where the experiments have thrown light upon the phenomenon of adsorption.

Clean-up of Hydrogen. (3)

When a tungsten filament is heated to temperatures of 1500°K in hydrogen at about 20 baryes pressure, the hydrogen slowly disappears, the pressure decreasing with time as indicated in curve I of Fig. 1. The pressure falls to a very low value in 10 to 20 minutes. If more hydrogen is introduced, the rate of clean-up is somewhat slower, the pressure decreasing according to curve II. Although analysis shows the residual gas to be pure hydrogen, the clean-up gradually comes to a standstill.

With a bulb containing 2 filaments, it is found that the lighting of the second filament does not cause a recovery in the rate of clean-up. This proves that the gas which disappears is not taken up by the filament itself. By keeping the bulb in liquid air, a greater total amount of clean-up is obtained. Such investigations show that the hydrogen which disappears becomes adsorbed on the surface of the bulb, but that the bulb is capable of adsorbing only a limited amount of hydrogen. This hydrogen adsorbed on the glass is capable of reacting with oxygen at room temperature after the filament has been allowed to cool. The adsorbed hydrogen is therefore in a chemically very active state. It was finally proved that the heated tungsten filament dissociates (4, 5, 6, 7, 8) a small fraction of the incident hydrogen molecules into atoms, and that these atoms, because of their unsaturated chemical nature, exhibit a strong tendency to be adsorbed on glass. These hydrogen atoms, however, are capable of reacting with one another and forming molecules. From this point of view, it should be impossible to hold on the glass more hydrogen than could form a layer one atom deep.

By cooling the bulb in liquid air the adsorption increased. The maximum amount of hydrogen adsorbed on the glass in these experiments was 0.03 mm^3

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

per cm² measured as molecular hydrogen at atmospheric pressure. This corresponds to $\sigma = 1.5 \times 10^{15}$ atoms of hydrogen per cm², which is equal to the number of spheres of diameter[1] 2.8 A which can be packed per cm² into a close-packed hexagonal lattice. The spacing of the adsorbed atoms is probably determined by the arrangement of the atoms in the underlying glass which provide "elementary spaces" in which atoms can be held. If the average diameter of the atoms of the glass can be assumed to be 2.8 A, the observed maximum amount of adsorbed hydrogen thus agrees well with that to be expected in a monatomic film. If a glass surface saturated with atomic hydrogen at liquid air temperature is allowed to warm up to room temperature, part of the hydrogen escapes as molecular hydrogen; the rest can be driven off at 300°C. Since adsorbed hydrogen atoms probably react on contact to form molecular hydrogen, then experiments indicate that the surface mobility of the adatoms[2] is very small at room temperature.

It was shown that the atomic hydrogen can diffuse long distances through glass tubing at room temperature (but not at liquid air temperature) and can then reduce metallic oxides (9), such as WO_3, CuO, Fe_2O_3, ZnO or PtO_2, and can dissolve in platinum sufficiently to raise its resistance (10). It reacts at room temperature with phosphorus (3) to form PH_3.

Oxygen Films on Tungsten.—When a tungsten filament is heated to 1500°K or more in oxygen at very low pressures, such as 100 baryes or less, the oxygen reacts (11) with the tungsten to form the oxide WO_3 which evaporates from the filament at these temperatures as fast as it is produced, leaving the surface of the filament apparently clean. At temperatures below about 2200°K the presence of extremely small amounts of oxygen (10^{-6} mm) decreases the electron emission from a tungsten filament to values that range from 10^{-2} to 10^{-5} of that from pure tungsten, depending on the temperature at which the emission is measured. This modification of the properties of the surface must depend upon the presence of a film which contains oxygen. When the filament temperature is high, such as 2000° or more, the emission returns to a normal tungsten emission as soon as the oxygen is completely consumed or is removed by vaporizing into the bulb a "getter" such as magnesium. If, however, the filament temperature is as low as 1500°, complete removal of oxygen from the gas phase, even by introducing caesium vapor as a getter, does not remove the oxygen film on the tungsten surface after it has once been formed. This means that the oxygen from such a film does not evaporate appreciably at 1500°K. Measurements at higher temperatures show that about half of the adsorbed oxygen evaporates in 27 minutes' time at 1860° and in about 20 seconds at 2070° (12). From the temperature coefficient at this rate of evaporation it

[1] Atomic and molecular distances will be given in terms of the Ångström unit 10^{-8} cm, which will hereafter be denoted by A.

[2] J. A. Becker, *Trans. Am. Electrochem. Soc.* **55**, 153 (1929), has suggested this term for adsorbed atoms.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

can be concluded that it will take about 3 years at 1500° to remove half the film by evaporation and that the heat of evaporation is of the order of 160 K cal. per gram atom.

This heat of evaporation is far greater than the heat of dissociation of oxygen into atoms; so we have very direct evidence that the forces that hold oxygen to a tungsten surface are comparable to the most powerful chemical forces known. This gives reason for believing that the oxygen film which so greatly decreases the electron emission from tungsten consists of a single layer of oxygen atoms which are chemically combined with the underlying tungsten atoms.

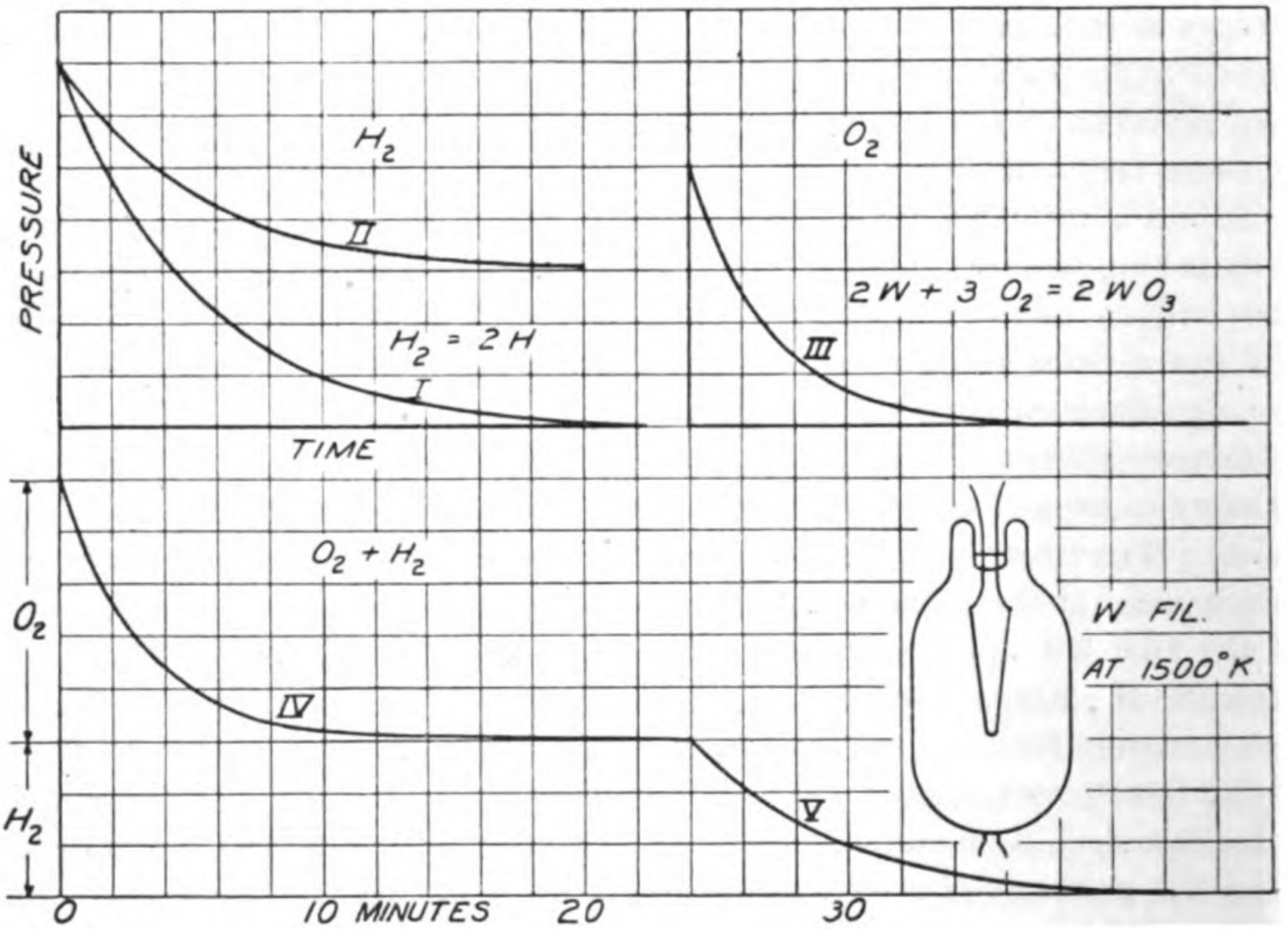


FIG. 1. Clean-up of hydrogen and oxygen in a tungsten filament lamp.

The electron emission from the tungsten filament in the presence of oxygen at temperatures below 1800° is found to be independent of the pressure of oxygen, provided that more than about 10^{-3} barye is present. This must mean that the surface is practically completely covered with oxygen and that an increase in oxygen pressure does not cause the thickness of the layer to increase beyond that of a single layer of atoms.

Curve III in Fig. 1 indicates the way in which the pressure of oxygen in the bulb decreases with time when the tungsten filament is maintained at 1500°K. The rate of disappearance of the oxygen is proportional to the oxygen pressure and there is no fatigue effect, such as was observed during the clean-up of hydrogen.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Interaction of Oxygen with Hydrogen in Contact with Tungsten Filament.— Mixtures of oxygen and hydrogen at low pressures in a bulb containing a tungsten filament behave in an extraordinary manner (See Ref. 13, p. 2271; Ref. 14; and Ref. 15, p. 608). Typical results obtained with a filament temperature of 1500° are shown in Curves IV and V of Fig. 1. These curves were obtained with a mixture of 3 parts of hydrogen and 5 parts of oxygen. When the filament was lighted, the gas disappeared at exactly the same rate as shown in Curve III when 5 parts of oxygen alone were present. After about 14 minutes practically all of the oxygen had disappeared. This was confirmed by analysis of the residual gas which was found to be pure hydrogen. This hydrogen, however, did not dissociate in the usual way into atoms and disappear by adsorption on the glass walls as shown in Curve I, but the pressure remained practically constant until after about 24 minutes, when the pressure suddenly began to decrease as indicated by Curve V. This Curve V, however, is identical with Curve I, which is characteristic of the clean-up of hydrogen in absence of oxygen. Repeated experiments with different amounts of oxygen and hydrogen prove that hydrogen does not interfere with the clean-up of oxygen but that a minute trace of oxygen of about 10^{-3} barye completely prevents the dissociation of hydrogen into atoms by a tungsten filament at 1500°K. The oxygen thus acts as a catalytic poison. Experiments of this kind can be used to make quite accurate chemical analyses of mixtures of oxygen and hydrogen.

The fact that a monatomic film of oxygen on tungsten does not react with hydrogen at 1500° is a striking indication that the oxygen is in a condition far different from that of gaseous oxygen. The results, however, confirm our conclusion that the film consists of oxygen atoms which are chemically saturated by the tungsten atoms with which they are in contact.

In view of the fact that an oxygen film on tungsten at 1500°K does not evaporate in less than a year, it is remarkable that in the presence of hydrogen the beginning of the hydrogen clean-up (Curve V) is so sharp. Since Curve V is exactly like the lower part of Curve I, it appears that once the hydrogen begins to dissociate, the oxygen is suddenly completely removed from the surface; in other words, hydrogen can remove monatomic oxygen films from the tungsten surface if the amount of oxygen on the surface is less than a definite amount. This probably means that the adsorbed oxygen molecules cannot react with hydrogen atoms directly but can react with hydrogen atoms adsorbed in adjacent spaces on the tungsten surface.

Thorium on Tungsten (16).—When a tungsten filament which is made from tungstic oxide containing about 1 per cent of ThO_2 is heated to temperatures of 2800° or more, a minute fraction of the thoria is reduced to metallic thorium. The thoria exists in the filament in the form of minute spherical particles distributed throughout the tungsten crystals and not at the boundaries of crystals. If the filament is then heated for a period of a few minutes at 1900 to 2000°K, the metallic thorium which has been produced at the

Digitized by Google Original from UNIVERSITY OF MICHIGAN

higher temperatures diffuses slowly through the crystal grains to the crystal boundaries, then diffuses rapidly along these boundaries to the surface of the filament and then spreads over the surface of the filament by surface migration and forms a monatomic film of adsorbed thorium atoms on the surface of the filament. At 2000° the rate of evaporation of thorium from the filament is so small that sufficient thorium soon accumulates on the filament to form a nearly complete monatomic film. If the temperature is raised to 2200 or 2400°, the rate of evaporation of the thorium from the surface increases so much more rapidly than the rate of arrival from the interior by diffusion, that the actual surface concentration decreases greatly.

These changes in the thorium content of the adsorbed film can be studied by measurements of the electron emission from the filament at a standard low temperature, called the testing temperature, which is chosen so low that neither diffusion to the surface, nor evaporation from the surface, causes appreciable changes in the adsorbed film. A convenient testing temperature is 1500°. At this temperature the presence of adsorbed thorium on the surface may increase the electron emission as much as 10^5 fold over that from a pure tungsten surface.

Such experiments make it possible to investigate the electrical properties of surface films having known amounts of thorium. On the assumption that each thorium atom on the surface acts as a dipole having a definite dipole moment, it is possible to show that the logarithm of the electron emission should increase linearly with the number of thorium atoms on the surface. The experiments showed that for low concentrations of thorium this relation holds approximately.

There are several indications that the adsorbed film of thorium that is formed by diffusion from the interior never exceeds one atom in thickness.

The Interaction of Carbon Dioxide with Carbon Filaments.—If a carbon filament is heated to a temperature above 1700°K in the presence of carbon dioxide at low pressure, one molecule of carbon monoxide is liberated from every molecule of carbon dioxide (See Ref. 2, p. 1154). If this carbon monoxide is pumped out from the bulb and the filament is then heated to 2300°K, a volume of carbon monoxide is slowly liberated equal to that originally formed from the dioxide. This proves that each carbon dioxide molecule which comes in contact with the filament and reacts, loses one oxygen atom to the filament and thus produces a carbon monoxide molecule. The oxygen atoms thus transferred to the filament form a monatomic film of oxygen atoms covering the surface, these atoms being chemically combined with the carbon atoms with which they are in contact, presumably by double bonds. This adsorbed film on the filament is very stable at 1700°, but when heated to 2300°, the film is destroyed, not by the evaporation of the oxygen atoms, but by the breaking of the bonds between the carbon atoms

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

which are attached to the oxygen and the underlying carbon atoms with which they are in contact. Thus the oxygen escapes as carbon monoxide.

From this point of view we see that we can look upon the adsorbed film on the carbon filament either as consisting of adsorbed oxygen, or as an adsorbed film of oriented carbon monoxide molecules, or as carbonyl radicals which are chemically attached by their carbon atoms to the underlying carbon atoms in the filament. It is to be expected that the properties of the adsorbed film would be very different if it consisted of carbon monoxide molecules attached to the underlying surface through their oxygen atoms. These experiments thus led to the concept that the properties of adsorbed films should in general depend on the orientation of the molecules or radicals in the film. It seemed to the writer (in 1915) that evidence of such orientation could be found among the data on the surface tensions of pure liquids.

Surface Energies of Pure Liquids (17) (18)

If a prism of liquid having a cross section of 1 sq. cm is divided into 2 parts by an imaginary plane perpendicular to the axis of the prism, and the 2 portions of the liquids are then separated, there has been an increase in the surface of the liquid of 2 sq. cm. The total energy theoretically required per sq. cm of new surface to bring about this separation may be called the total surface energy γ_0. This is related to the free surface energy γ, which is equivalent to the surface tension of the liquid, by the relation

$$\gamma_0 = \gamma - T\frac{d\gamma}{dT}.$$

By measurements of the surface tension, the surface energy γ_0 can thus be measured. This quantity represents the potential energy of the molecules which form the surface of the liquid (per sq. cm) in excess of that which the same molecules possess when they are in the interior of the liquid.

In Table I data are given for a few substances which serve to illustrate the interrelation (19) (20) between the orientations of molecules and other properties of liquids. The latent heat of evaporation, λ, which, according to Trouton's Rule, is approximately proportional to the absolute boiling point, T_B, serves as a measure of the energy needed to bring a molecule from the interior of the liquid out into the vapor phase. We have seen that the surface energy γ_0 is the energy per unit area needed to form a surface.

The molecular volume V given in this table is the volume of the liquid divided by the number of molecules. The molecular surface S is the surface of a sphere which has the volume V. The extremely low values of λ, the heat of evaporation, per molecule, for helium and hydrogen, indicate that the forces exerted by these molecules on their neighbours are unusually weak. This is in accord with the great stability of the electron pair which forms

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the K shell of atoms and the covalence bond. The diameters of the helium atom and hydrogen molecule given by the kinetic theory from viscosity measurements, viz., 1.9 and 2.4 A, correspond to volumes V of only 3.6 and

TABLE I

Surface Properties of Molecules

Substance Unit =	V Volume A³	S Surface A²	T_B Boiling point °K	λ Heat of evaporation Erg × 10^{-14}	λ/S Erg cm^{-2}	γ_0 = Erg cm^{-2}
He	52.	68.	4.3	0.24	0.35	0.59
H—H	47.	63.	20.5	1.67	2.7	5.4
H—OH	30.	48.	373.	67.	140.	118.
A	47.	63.	88.	11.3	18.	35.3
CH_4	64.	78.	112.	16.3	21.	—
n-C_5H_{18}	266.	200.	393.	56.	28.	50.7
n-$C_8H_{17}OH$	260.	198.	467.	82.	41.5	50.7

7.2 A³, which are very small compared to the volumes occupied in the liquid. This very open structure of the liquid is again an indication of the weak attractive forces between these molecules.

The effect of replacing one of the hydrogen atoms in the hydrogen molecule by the hydroxyl radical, thus producing water, is to decrease the value of V from 47 to 30, an indication of strong forces acting between the hydroxyl groups which compress the liquid. A better measure of these forces is given by the 40-fold increase in the value of λ from 1.67 to 67. The surface energy γ_0 has been increased 24-fold.

The data for argon illustrate the properties of an atom having a complete electron shell or octet. The fact that in spite of the much larger electron configuration (with a kinetic theory diameter of 2.9) the volume per molecule in the liquid is the same as for hydrogen, shows that the field of force around the molecule is far greater than for hydrogen and helium. The heat of evaporation per unit area λ/S is a very convenient measure of the intensity of this field. With H_2, He and A it is about one-half of the surface energy γ_0.

The data for methane indicate that this molecule has a value of λ/S, about the same as that for argon. This molecule has a completed octet which shares pairs of electrons with hydrogen atoms. Evidently the presence of the hydrogen atoms does not appreciably alter the field of force; the main effect is to raise the molecular volume, thus raising λ and the boiling point T_B almost in proportion to S.

The values for λ/S for the saturated aliphatic hydrocarbons beyond propane are practically constant and equal to 28. The same constancy is shown

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

in the surface energy γ_0. The data for octane shown in the table are typical. The surfaces of the molecules of the higher saturated hydrocarbons are thus very much like those of argon atoms, the effect of the chain formation manifesting itself principally in the increase in λ/S from 18 to 28.

The constancy of λ/S is also an indication that the molecules of the vapors of the higher hydrocarbons are approximately spherical in form. The known flexibility of the chain and the surface energy reduction resulting from the more compact form afford ample explanation of this spherical form.

The effect of substituting a hydrogen atom in octane by a hydroxyl radical is illustrated in the last line of the table by the data for *n*-Octyl alcohol. There is a small decrease in V paralleling that observed in H_2O, except that now, since each OH group in the liquid cannot be close to many other OH groups, the decrease in volume is considerably less. The large field of force around the OH group is best illustrated by the increase of 26 units in the value of λ. The fact that this increase is less than half of that observed in the change from H_2 to H_2O shows that the OH group in the molecule of the vapor of octyl alcohol is able to bury itself, at least in part, in the approximately spherical molecule.

In spite of the large increase in λ and λ/S in octyl alcohol, the surface energy γ_0 is the same as for octane. This can be explained by the ***orientation of the molecules*** in the surface layer of octyl alcohol. The great attractive forces exerted by the hydroxyl groups causes them to be drawn down into the interior of the liquid. Thermal agitation tends to counteract this tendency. According to the Boltzmann equation the relative distribution of molecules between two regions of differing energy is measured by exp (W/kT), where W is the difference in the energy of the molecule in the two states. Now, judging from a comparison of the values of λ for octane and octyl alcohol, the energy necessary to bring an OH group from a hydrocarbon environment out into free space is at least 26×10^{-14} erg. The energy corresponding to kT at room temperature is about 4×10^{-24} erg. Since W is thus more than 6.5 times as great as this, we may conclude that nearly all of the molecules [all but about exp $(-6.5) = 10^{-3}$] in the surface of octane will be oriented in such a way that the hydroxyl groups do not reach the surface.

We may now understand why the surface energy of octyl alcohol is the same as that of octane. We have previously seen that γ_0 can be determined by the energy needed to separate a prism into two parts. We may conceive of this separation as taking place in two steps. The molecules on the opposite sides of an imaginary dividing plane may first be oriented so that the hydroxyl groups are turned away from this plane, leaving only the hydrocarbon parts of the molecule in contact with the plane surface. The two bodies of liquids are then separated from each other along this plane, which would require only the same energy as for pure octane. Because of the orientation of the molecules, γ_0 thus differs from that of octane only by the amount

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of energy needed to turn the molecules around in the interior of the liquid, which is probably negligible.

Referring again to Table I we see that a comparison of λ/S with γ_0 affords a measure of the effect of orientation. In general, for molecules with uniform fields of force, λ/S is from 0.5 to 0.55 of the value of γ_0.

When, however, a part of the molecular surface has a much weaker field of force than that of other parts, the surface of the liquid consists principally or wholly of the least active parts, so that γ_0 is lower than normal. Thus for octyl alcohol λ/S is 0.82 of γ_0 while for water it is 1.18, indicating that the water molecule is very unsymmetrical and is strongly oriented at the surface.

At present these illustrations will suffice. In a paper published in 1916 I showed that this theory was applicable to the surface tension of organic liquids in general, including cases of substituted benzene derivatives where the values of γ_0 depend to a marked degree on the relative positions of the substituted groups. Somewhat later W. D. Harkins and his co-workers investigated large numbers of organic substances in this way and completely demonstrated the importance of orientation of molecules in the surface layer of liquids consisting of unsymmetrical molecules.

Oil Films on Water (18) (21)

When a pure saturated liquid hydrocarbon is placed upon the water, it remains on the surface as a drop or lens which has no effect on the surface tension of the surrounding water. If, however, an insoluble fatty or oily substance, such as the common vegetable and animal oils, is placed upon clean water, it spreads out almost instantly as a thin film over the surface. If the motions of the surface are made visible by dusting the surface with powdered talc, it may be seen that, with a limited amount of oil, the film only spreads out sufficiently to cover a definite area, or at least if the area exceeds a rather definite value, the oil has no effect on the surface tension of the water. A comparison of various insoluble organic substances has proved that the spreading tendency depends upon the presence of certain active groups or radicals in the organic molecule, these being the groups which tend to increase the solubility of organic substances in water. For example, pentane, C_5H_{12}, is practically insoluble in water but amyl alcohol, $C_5H_{11}OH$, is relatively soluble. Thus the OH groups in organic molecules exert strong attractive forces on the OH groups in the water molecules and these manifest themselves by an increase in solubility. Similarly the carboxyl group COOH tends to make the lower fatty acids much more soluble in water than the corresponding hydrocarbons.

Hydrocarbons with high molecular weight such as $C_{18}H_{38}$ are extremely insoluble in water. If the carboxyl group replaces the CH_3 group at the end of the chain $C_{18}H_{38}$, one end of the molecule only tends to dissolve in water,

Digitized by Google Original from UNIVERSITY OF MICHIGAN

whereas the rest of the molecule still retains the insolubility of the hydrocarbons. By spreading over the surface of the water, molecules of this kind can bring their carboxyl group in contact with the water without separating from one another.

An oil film formed in this way must consist of a single layer of molecules packed closely on the surface layer of the water. If there is a surplus of the fatty acid, as compared with the limited area over which it can spread, the endeavor of the carboxyl groups to come in contact with water causes the molecules to become so crowded at the surface that they stand nearly erect, side by side on the surface. The area occupied by each molecule is thus determined by the cross section of the hydrocarbon chain or by that of the head in contact with water, if this happens to be larger than the cross section of the chain. The thickness of the film is then determined by the length of the hydrocarbon chain.

By dissolving known weights of liquid or solid, oily or fatty substances in a volatile solvent such as hexane, and placing known amounts of these dilute solutions on the water surface, a definite number of molecules can be transferred to the water surface. The oil film can be confined to a given portion of the surface of water in a long tray by a floating strip of paper reaching across the tray. By measuring the forces exerted on the strip of paper, it is possible to measure directly the spreading force F in dynes per cm exerted by an oil film having a given number of molecules of oil per square cm of surface. This surface concentration we shall denote by the symbol σ. Such measurements as these, by which F can be expressed as a function of σ and T, give us then the 2-dimensional equation of state of the oil film which corresponds exactly to the 3-dimensional equation of state which characterizes ordinary gases and liquids. In fact, the movable paper strip in these experiments is the equivalent of a piston which compresses the gas in a cylinder.

The oil films observed on water may exist as 2-dimensional solids, liquids or gases. The film on water obtained from stearic acid $C_{17}H_{35}COOH$ is solid. If it is compressed by a force of 10 dynes per cm exerted against the paper strip, this solidity is manifested if particles of talc are dusted on to the surface and the effects of air currents directed against the surface are watched. The talc particles do not move freely over the surface; if a strong wind displaces them, they return to their original positions when the wind stops, proving a surface rigidity and elasticity characteristic of solids. Other substances such as cetyl alcohol or oleic acid give films which are liquid, since talc particles circulate freely when small forces are exerted by the wind.

By slightly increasing the area available for these films of saturated fatty acids, it is found that the spreading force decreases very nearly to zero, which proves that these films do not act as 2-dimensional gases but rather as 2-dimensional liquids which have an unmeasurably small 2-dimensional vapor

Digitized by Google Original from UNIVERSITY OF MICHIGAN

pressure. With myristic acid (22), however, a definite 2-dimensional vapor pressure of about 0.2 dyne cm^{-1} is observed. Still lower fatty acids give typical gaseous films, but they cannot be studied by this method because the films are so easily soluble in water that the force exerted by a moving barrier causes them to go into solution.

Adsorbed Films on Solutions (18) (21).—The foregoing method for studying the properties of oil films on water is inapplicable if the film is soluble or is volatile. In such cases measurements must be made in the presence of saturated vapor or saturated solution. Gibbs' equation, Eq. (1), gives us a means of determining the relation between the amount adsorbed on the solution and the spreading force F, in terms of the partial pressure p of the vapor of the adsorbed substance over the liquid or the partial osmotic pressure p of the dissolved substance in the underlying solution. Experimentally F can be measured as the decrease in the surface tension of the pure liquid produced by the presence of the dissolved substance. By the integration of this equation, using the experimentally determined values of F, one can obtain the equation of state of the 2-dimensional film whether this is gaseous or liquid or solid.

For very high or very low surface concentrations, Gibbs' equation takes simple limiting forms. At very low concentrations the molecules in the adsorbed films are so far apart that they exert no appreciable forces on one another. Under such conditions σ, the surface concentration, will be proportional to the volume concentration which in turn is proportional to p. If we solve Eq. (1) on the assumption that σ is proportional to p, we find that it leads to the following equation of state

$$F = \sigma kT, \tag{6}$$

which is the 2-dimensional analogue of Eq. (3), the equation of state of an ideal gas, and it may therefore be called an equation of state of an ideal 2-dimensional gas.

The effect of forces acting between the adsorbed molecules is to modify this equation. A 2-dimensional analogue of Van der Waals' equation can be written in the form

$$F = \frac{\sigma kT}{(1-\sigma/\sigma_1)} + a\sigma^2, \tag{7}$$

where a and σ_1 are constants.

When the gas phase or the liquid phase contains a relatively high concentration, the concentration of the molecules in the adsorbed film tends to increase to a limiting value σ_1 corresponding to a complete monomolecular adsorbed film such as those that we observed in the study of oil films on water. Although such films show surface elasticity, that is, they are compressible, the forces required to compress the liquid and solid films are so much

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

greater than those required to compress the gaseous film, that the surface compressibility can be neglected as the first approximation, so that we can consider σ_1 to be approximately constant, that is, independent of p and F. Making this substitution in Eq. (1) and integrating, we obtain the following equation which should be applicable for concentrated surface films

$$F = \sigma_1 kT \ln (p/p_0). \tag{8}$$

These two limiting equations are completely in accord with the general relationships found by J. Traube (23). In Eq. (8) p_0 is an integration constant whose value cannot be found from Gibbs' equation.

From the Boltzmann equation we can estimate the energy change λ involved in bringing a molecule from the vapor or liquid phase to the surface phase. We thus have

$$\sigma/p = \text{const} \exp (\lambda/kT). \tag{9}$$

Traube found that with molecules of aliphatic compounds having different lengths of hydrocarbon chains, the ratio F/p for dilute solutions (which should be proportional to σ/p) increases about 3-fold for each CH_2. When this is interpreted in accord with Gibbs' and Boltzmann equations, we conclude that the energy λ involved in the adsorption of these molecules increases linearly with the length of the chain. This means that each CH_2 group in the molecule must be similarly situated in the surface film. In other words, in these dilute films where there is much free water surface available, the hydrocarbon molecules must lie flat on the surface. With the concentrated films in which σ is constant so that Eq. (8) applies, there is no available free surface of water and the molecules must stand nearly erect on the surface.

These two cases given by Eqs. (6) and (8) are only limiting cases and the complete equation of state for the whole range from dilute to concentrated films would be more complicated, since it must involve the intermediate states between those in which the molecules lie flat on the surface and stand erect on the surface. The experimental difficulties of the accurate measurements of the surface tensions of solutions are such, that relatively little work has been done on the equation of state of these adsorbed films on solutions as compared with the large amount of work done by N. K. Adam (22) and others on the equations of state of films of insoluble substances on water.

The molecules in adsorbed films on liquids are of course free to move over the surface of the liquid except in so far as the film itself may possess the properties of a solid.

Adsorbed Films on Solids.—Adsorbed films on solids may exist in three states corresponding to 2-dimensional gases, liquids or solids. A new factor now appears, however, which was not present in the case of adsorbed films on liquids. The forces exerted by the underlying solid on adsorbed atoms or molecules tend to hold the molecules in definite positions fixed by the

Digitized by Google Original from UNIVERSITY OF MICHIGAN

lattice of the solid. The solid surface is thus to be looked upon as a type of checkerboard containing definite numbers and arrangements of elementary spaces (13) (24), each of which is capable of holding an adsorbed molecule. To move a molecule from one elementary space to another thus presumably requires something analogous to an activation energy; only those molecules possessing a sufficient kinetic energy to pass over a potential barrier can succeed in hopping from one elementary space to another (25). On this basis we should expect a surface mobility at high temperatures which would disappear at low temperatures. The logarithm of the rate of mobility, or the surface diffusion coefficient, should vary linearly with the reciprocal of the absolute temperature and the slope of this line should be proportional to the activation energy.

In general the surface diffusion coefficient increases with σ, for the ability of adatoms to cross the potential barrier is not determined solely by the thermal agitation of the molecules but depends on $dF/d\sigma$, since differences in the value of F over the surface contribute to the mobility.

We may thus consider that in general the adatoms on solids move over the surface by hopping between elementary spaces. If the adatoms move nearly independently of one another, so that they migrate freely on to all unoccupied portions of the surface, the adsorbed films can be regarded as a 2-dimensional gas in spite of the fact that the atoms tend to occupy definite positions. Such films constitute a 2-dimensional crystalline gas, the crystalline character being imparted by the underlying lattice. If attractive forces exist between the adatoms which are sufficiently strong to cause them to form a definite 2-dimensional condensed phase in equilibrium with a 2-dimensional vapor phase, we clearly have to do also with a 2-dimensional solid or liquid. If the mobility is high, this condensed film may have properties characteristic of liquids; with no mobility at lower temperatures, the conditions will be analogous to that of a 2-dimensional glass. A 2-dimensional solid analogous to ordinary 3-dimensional solids would exist only if the forces exerted by the adatoms on each other can keep them from slipping past one another.

Condensation-Evaporation Theory of Adsorption on Solids.—When molecules of a gas in contact with a solid impinge individually on the solid, they may either condense or may rebound from the solid as though elastically reflected. Those molecules that condense may subsequently evaporate. There is much theoretical and experimental evidence that a true reflection of molecules under these conditions is a rather abnormal occurrence, although the specular reflection of molecular rays from certain crystalline surfaces shows that it sometimes exists. In the great majority of cases, however, the observed phenomena indicate that the larger part of all incident molecules condense on the surface and reach thermal equilibrium with it before they evaporate (26) (27). With such gases as hydrogen and helium accommodation coefficients materially less than unity have been found. In general these occur with gases striking

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

solids at such temperatures that the rate of evaporation may be assumed to be so high that the life of the condensed molecule is of the order of 10^{-13} seconds, which is about the time required for a molecule to perform a single thermal oscillation on the surface. Under these conditions it is not surprising that thermal equilibrium is not reached.

When the rate at which molecules impinge on the surface is μ, as given by Eq. (4), and ν is the rate at which they evaporate (molecules cm^{-2} sec^{-1}), then the rate at which they accumulate on the surface is given by

$$\frac{d\sigma}{dt} = \alpha\mu - \nu, \tag{10}$$

where α, the condensation coefficient, in the majority of cases is equal to unity, but in any case can never exceed unity. The rate of evaporation ν is in general dependent on the temperature and on σ, the surface concentration. Of course it also depends on the nature of the solid surface on which adsorption occurs. If the surface is strictly homogeneous, ν may be a function of σ and T only for a given surface, but it may be possible that different portions of the surface are capable of exerting different forces on adatoms, so that ν and σ may not be uniform over the surface.

In a stationary state when σ is not changing with time, the general condition that must be fulfilled is

$$\alpha\mu = \nu, \tag{11}$$

If we divide the rate of evaporation ν by σ, the number of atoms per square cm, we obtain the average probability per second for the evaporation of the individual atoms. The reciprocal of this, τ, is thus the average life of an adatom on the surface. Thus we have

$$\tau = \sigma/\nu. \tag{12}$$

This time lag that exists between the condensation and the evaporation of adatoms may thus be looked upon as the fundamental cause of the adsorption of gases on solid surfaces.

In general ν should increase rapidly with temperature like the vapor pressure of substances. Thus the logarithm of ν should increase approximately linearly when plotted against the reciprocal of the absolute temperature, and the slope of this line is proportional to the heat of evaporation and is a measure of the magnitude of the forces by which the adatoms are held on the surface. Thus ν should be approximately given by an equation of the type

$$\nu = \text{const. exp } (-\lambda/kT), \tag{13}$$

where λ is a measure of the energy required to remove an adatom from the surface. The reason for the large variations of ν for different substances is due mainly to variations of λ rather than to differences (28) in the constant factor in Eq. (13). This is indicated by such approximate laws as Trouton's rule.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The forces acting between atoms and molecules are normally of extremely short range (27) (29), so that the forces acting on an adatom, which determine the magnitude of λ, and therefore of ν, depend mainly upon the atoms with which any given adatom is in contact. When the gas pressure is raised or the temperature is lowered so that σ increases to such a point that there is no longer room for any additional molecules in the first layer in contact with the solid, a still further increase in σ would require that a large number of adatoms must be contained in a second layer. Now these adatoms in the second layer cannot be in *contact* with the solid surface on which the primary adsorption occurs, and therefore for these atoms λ_2 should differ from the value of λ_1 that applies to the adatoms in the first layer. Since λ occurs in the exponent of Eq. (13), a relatively small change in λ is sufficient to cause a marked difference in the value of v.

Thus when the adsorbed substance is not nearly identical in its properties with the substance on which adsorption occurs, we should expect the value of ν for atoms in the first and atoms in the second layer to be greatly different from one another. Naturally two cases may arise: ν_2 may be either greater or less than ν_1. (Ref. 28, pp. 2811 and 2815).

Case 1. $\nu_2 < \nu_1$.—If ν_2 is less than ν_1, the atoms in the second layer are held by stronger forces to those in the first layer than these latter are by the atoms of the underlying solid. There is therefore a tendency for the atoms in the first layer to form clusters and on these clusters the second and third, etc., layers begin to form long before the whole of the first layer is covered (27). Such phenomena are of common occurrence. For example, when mercury, cadmium or iodine is vaporized in vacuum and is condensed on a glass surface, at a not too low temperature, discrete crystals of the condensed substances form on the glass. This is a direct indication that these atoms exert greater forces on one another than they do on the underlying glass.

If the glass surface is maintained at a temperature so high that these nuclei do not form, then the glass surface *appears* to reflect all the incident atoms, for they evaporate from the glass surface far more rapidly than they do from a cadmium surface at the same temperature. Such observations were made by R. W. Wood, who attempted to explain them by a large reflection coefficient. He believed that experiments indicated that molecules of mercury incident at low pressures on cold glass surfaces were completely reflected at temperatures above —90°C, but were completely condensed below that temperature.

From our present viewpoint such a critical temperature has nothing to do with a true reflection but is dependent on the fact that with a given stream of mercury or cadmium atoms there is a definite temperature below which evaporation of the individual adatoms cannot take place fast enough to prevent accumulation sufficient to form a monatomic film, so that all further evaporation at these low temperatures ceases. Experiments show conclusively that at all temperatures the mercury atoms condense, but that, if the temperature

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

conditions are favorable, single atoms reevaporate from the glass at fairly low temperatures.

It is evident therefore that those cases in which ν_2 is less than ν_1 are characterized by the growth of crystals from nuclei and do not lead to the formation of monomolecular films but rather to discrete crystal particles.

Case 2. $\nu_2 > \nu_1$.—In this case, as the pressure is gradually raised or the temperature is lowered, σ increases until a monomolecular film is formed, but it then takes a considerable decrease in temperature or increase in pressure before a second layer begins to form. These conditions therefore commonly lead to the formation of films which do not exceed a molecule in thickness over a wide range of experimental conditions. This case therefore is characterized by typical adsorbed films.

Adsorption Isotherms.—The fundamental equation governing the amount of adsorbed substances on a solid surface is given by Eq. (11). To put this into a definite form relating the pressure p of the external gas and σ, the surface concentration, we need only to be able to express α and ν as functions of σ and T. The functional relation of ν to σ depends not only on the forces exerted by the underlying solid, but on the forces acting between adatoms. Furthermore we must consider that the incident molecules corresponding to μ cannot all go directly into elementary spaces on the bare surface, but many of them will make their first contact at places already occupied by adatoms. An important aspect of the problem of the adsorption isotherm is the determination of the manner in which these incident atoms find places in the first layer. Many atoms may temporarily be forced to occupy places in the second layer from which they can either evaporate at a much higher rate than from the first layer, or may migrate until they drop into positions in the first layer.

It is natural under these conditions to make assumptions which are as simple as possible and to see whether the resulting equations can find a field of application (24). If the adatoms do not exert appreciable forces on one another, we may thus assume that the life of τ of each one is independent of the presence of other atoms on the surface. Thus by Eq. (12) ν is proportional to σ.

Instead of dealing with the surface concentration of σ it is often convenient to use the covering fraction Θ defined by

$$\Theta = \sigma/\sigma_1, \tag{14}$$

where σ_1 is the surface concentration in a complete monomolecular film.

Thus we may put

$$\nu = \nu_1\Theta, \tag{15}$$

where ν_1 represents the rate of evaporation from a completely covered surface.

When molecules incident on the surface strike a part which is unoccupied by other adatoms, we may assume that the fraction α_0 condenses. The fraction of such surface which is bare may be represented by $1-\Theta$. Therefore the number of incident atoms which go directly into the first layer may be

Digitized by Google Original from UNIVERSITY OF MICHIGAN

put equal to $a_0\,(1-\theta)\mu$. The fate of the other incident atoms, viz., those that first strike adsorbed atoms, will depend on many factors, some of which we shall discuss later. A very simple, although not very probable, assumption is that all these atoms reevaporate so fast that they do not have opportunities to find positions in the first layer. On these assumptions we find

$$a\mu = a_0(1-\theta)\mu. \tag{16}$$

Substituting this and Eq. (15) into Eq. (11) and solving for θ, we obtain the following simple adsorption isotherm,

$$\theta = \frac{a_0\mu}{\nu_1+a_0\mu}. \tag{17}$$

This equation has been found to apply with reasonable accuracy to a surprisingly large number of cases of adsorption on plane surfaces. Considering the nature of the simplifying assumptions made in its derivation, it should of course not be looked upon as a general equation for the adsorption isotherm. The cases where this equation is most likely to apply are those in which the adsorption occurs only in elementary spaces which are so far separated from one another that the adatoms in the separate spaces do not exert appreciable forces on one another. This can justify the assumption of Eq. (15). Also in this case the condensation may reasonably occur according to Eq. (16), because if a given space is occupied, which has a probability proportional to θ, the incident atom cannot merely slip into an adjacent elementary space but must fall on to an area on which it is held with so little force that it evaporates before it can move into any vacant elementary space. These assumptions will give us an equation like Eq. (17) except that the significance of θ and of the coefficient a_0 is somewhat modified.

Recent experiments have shown that in the mechanism of condensation mobility plays an important part (30). Thus in general an incident molecule striking a surface already covered may be assumed to move an appreciable distance before finally settling into a position in the first layer. Certainly if the surface is homogeneous so that all parts of it are available for adsorption, an incident molecule striking an isolated adsorbed molecule can hardly be regarded as being even temporarily in a second layer. Such an atom will slip into a position in the first layer before having any occasion to rebound or evaporate from the surface. An atom cannot be in a second layer even temporarily unless it is supported by at least three or more often four atoms in the underlying layer. Even if there is no mobility, the probability that an incident atom could occupy a place in the second layer would be proportional to θ^n, where n is at least as great as 3 or 4. If the rate of evaporation is very high, we might expect these atoms to evaporate before finding places in the first layer. On this basis, therefore, instead of Eq. (16), the expression for the rate of arrival of atoms in the first layer should be

$$a\mu = a_0(1-\theta^n)\mu, \tag{18}$$

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Some experiments were made to test the reasonableness of these conclusions. The bottom of a tray was covered with steel balls ($^3/_8$ inch diameter) closely packed into a square lattice and cemented into position. This surface thus possessed many of the features of a homogeneous crystal surface, the steel balls corresponding to the individual atoms. When other balls of the same size were thrown on to the surface, they occupied definite elementary spaces, each being in contact with four underlying balls. The number of such elementary spaces (except for an edge correction) was the same as the number of balls which were cemented into place (zero layer). A large number of balls, sufficient to cover the fraction θ of the available spaces, was placed in the tray (in first layer) and the tray was shaken to give a random distribution. A small number of additional balls were then dropped at random from a height of 5 cm to the surface, and the number of these which went into the second layer was counted. It was found that the probability P that a given incident ball would occupy a position in the second layer was quite accurately given by

$$P = \theta^{4.5}. \tag{19}$$

The fraction of the incident balls finding positions in the first layer was thus $1-\theta^{4.5}$. A comparison of this with Eq. (18) gives a value of $n = 4.5$. The reason that n is greater than 4, the number of underlying atoms, is probably that the kinetic energy of the balls causes some of them to roll from their positions of first contact.

Applying these results to adsorption, we should expect that, until θ is very close to unity, all atoms incident on the surface should reach positions in the first layer without any opportunity of evaporation or reflection, even if the evaporation rate in the second layer is very high.

Effect of Forces Acting between Adatoms (28).—The fact that 2 adatoms cannot occupy the same elementary space at the same time must mean that they exert repulsive forces on one another. This will manifest itself in the equation of state of the adsorbed atoms by a factor such as the $1-\theta$ in the denominator of the first term of the second member of Eq. (7). This means that the spreading force tends to rise indefinitely as θ approaches the value unity. Combining this equation of state with Gibbs' equation, and assuming $\alpha = 1$, we obtain for an adsorption isotherm the equation

$$\ln(\nu/\theta) = \ln[1/(1-\theta)]+1/(1-\theta)+\text{const.} \tag{20}$$

Thus we see that the rate of evaporation should increase indefinitely as θ approaches unity. It is just this effect which limits the amount of material in typical adsorbed films on liquids or solids to that contained in a monomolecular layer.

The forces holding adatoms on the surface in characteristic cases of adsorption are usually far greater than those acting between adatoms. If this were not the case, we would be dealing normally with the case in which ν_2 is less than ν_1, so that we would not have adsorbed films but crystal nuclei. The effect

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of these strong forces originating from the underlying surface is to polarize the adatoms. If these are all of one kind, they thus tend to become similarly oriented dipoles which repel one another with a force varying inversely as the fourth power of the distance between them. There may also be attractive forces of the Van der Waal's type, but these will vary with a much higher power of the distance. The dipole forces will have a range of action far greater than other forces involved. A knowledge of these factors which are probably important in most cases of adsorption can best be acquired by a detailed study of some one example in which quantitative determinations of all the factors are possible. The example that I have chosen for this purpose is that of adsorption of caesium vapor on tungsten, for in this case we can measure with great precision the surface concentration σ as well as the rates of evaporation ν of atoms, of ions, and of electrons (30). Thus we are able to express these values of ν_a, ν_p and ν_e as functions of Θ and T. These measurements enable us not only to determine the forces acting between the adatoms but also to determine the electrical properties of the adsorbed films.

Caesium Films on Tungsten.—The ionizing potential of caesium is 3.9 volts, which is lower than that of any other chemical element. The heat of evaporation of electrons from tungsten corresponds to 4.6 volts. Thus the energy necessary to detach an electron from a caesium atom is 0.7 volts less than that necessary to pull an electron out of metallic tungsten. It is therefore not surprising that experiments (31) (32) show that every caesium atom which strikes a tungsten filament at high temperature loses its electron and escapes as a caesium ion. The electric current that thus flows from the tungsten is a quantitative measure of the number of atoms of caesium that strike the filament. Since currents of 10^{-17} amps. can be measured by an electrometer, it thus becomes possible to detect a pressure of caesium vapor so low that only 100 caesium atoms per second strike the surface of a filament.

The escape of the caesium ions from the tungsten surface is an evaporation phenomenon. If the temperature is below about 1100°K, the rate of evaporation of the ions may be so low that it does not keep pace with the rate at which the atoms arrive, so that there is an accumulation of adsorbed caesium on the surface. As a matter of fact, the rate of evaporation of the adsorbed caesium from the surface at a thousand degrees is about the same as that from a surface of metallic caesium at room temperature (300°K). Thus from Trouton's Rule we should expect the heat of evaporation of caesium adatoms to be about three times as great as the heat of evaporation of caesium itself.

Such large forces between the adsorbed caesium atoms and the underlyign tungsten surface are to be expected as a result of the fact that the caesium tends to lose its electron when close to the tungsten surface. Thus the positively charged caesium ion induces into the conducting tungsten surface a negative charge, which exerts a force of attraction on the ion (the "image force") equal to $e^2/4x^2$, where x is the distance of the ion from the surface. This image force

Digitized by Google Original from UNIVERSITY OF MICHIGAN

is of ample magnitude to account for the strong forces holding caesium on tungsten.

If a thoriated tungsten filament is used, and this is given the special heat treatment required to bring a complete monatomic film of thorium to the surface, the heat of evaporation of electrons falls to about 3 volts, which is 0.9 of a volt lower than the ionizing potential of caesium. In accord with this fact the experiments show that caesium atoms are not converted into ions by an activated thoriated filament, nor is there any observable tendency for the caesium to become adsorbed on the filament.

If, with a pure tungsten filament in presence of caesium vapor, the temperature is maintained low enough to permit an adsorbed film of caesium to be formed, the positively charged adatoms, which cause a positive contact potential against the pure tungsten surface, have the effect of lowering the heat of evaporation of the electrons. When such an amount of caesium is present on the surface that the heat of evaporation is materially below 3.9 volts, the tendency of the filament to rob incoming caesium atoms of their electrons and thus allow them to escape as ions is lost. This means that ν_p, the rate of evaporation of ions, becomes very small as θ, the fraction of the surface covered by caesium atoms, increases.

At temperatures of about 700°K, in presence of caesium vapor saturated at room temperature (pressure about 10^{-9} atmospheres), θ increases to approximately 0.7 and the heat of evaporation has then been lowered to such a point that the electron emission is 10^{22} times greater than that of a clean tungsten filament at the same temperature.

Within the last three years, Dr. J. B. Taylor and I have made a detailed study (28) (30) of the rates of evaporation of atoms, ions and electrons from these caesium films on tungsten as functions of θ and T. In order to measure θ, a method was devised for determining σ, the number of adsorbed atoms per square cm of tungsten surface. Two methods were found. When θ is less than 0.08, a sudden heating or flashing of the filament at temperatures above 1300° causes every caesium adatom to escape from the filament as an ion so that the ballistic kick measured with the galvanometer gives directly the value of σ. The second method, which is applicable at any values of σ (even those corresponding to polyatomic layers), involves the evaporation of the adatoms as atoms, in the presence of a retarding field which prevents the escape of ions. This burst of atoms falls on a parallel neighbouring tungsten filament heated above 1300° from which these atoms escape as ions. The ballistic kick of current from this second filament thus measures σ on the first filament. We call this the 2-filament method of measuring σ.

The measurements of σ showed that as the caesium pressure is increased or the filament temperature lowered, σ increases to a definite limiting value of σ_1 which is 4.8×10^{14} atoms per square cm of apparent filament surface. A study of the crystal habits of tungsten has shown that the surface lattice

Digitized by Google Original from UNIVERSITY OF MICHIGAN

of surfaces etched by evaporation contains 1.425×10^{15} atoms per square cm. Since the diameter of the caesium atoms is almost exactly twice that of tungsten, and because of the tendency of the adatoms under the strong forces exerted by the tungsten, to occupy definite elementary spaces on the surface, we conclude that the maximum number of caesium adatoms is one quarter the number of tungsten atoms and therefore the true value of σ_1 is 3.563×10^{14} atoms per square cm. Comparing this with the observed or apparent value of σ_1 it appears that the true surface of the tungsten filament is 1.347 times the apparent surface, this difference being due to the slight etching of the filament surface by evaporation at high temperatures.

A study of transient states during which θ increases or decreases with time has proved conclusively that the phenomenon of condensation or evaporation go on independently of one another, the condensation being dependent on μ, while the evaporation ν is strictly a function of θ and T only, and does not depend upon the way the surface film has been formed.

The experiments show that within the accuracy of the experiments (about 0.5%) the condensation coefficient α is always equal to unity even when θ is as great as 0.98. This proves that the incident atoms, which under these conditions must nearly all strike adatoms, can slide around in a second layer until they find positions in the first layer. The experiments prove, however, that the number of atoms which exist at any time in the second layer is extremely minute, of the order of 10^{-7}. The atoms in the second layer possess very high surface mobility.

The rate of evaporation of atoms ν_a increases at any given temperature extremely rapidly as θ increases. Thus at 1000°K an increase of θ from 0.1 to 0.9 causes a 10^{11}-fold increase in ν_a. This indicates very strong repulsive forces between the adatoms in agreement with the fact that these adatoms tend to be positively charged as indicated by the effect of the film in increasing the electron emission. It has been possible to develop this relationship between ν_a and ν_e into a quantitative theory.

A single caesium adatom on a tungsten surface may be regarded as an ion held to the metal by its image force. The image and the ion thus constitute a dipole, having an electric moment M, oriented with its axis perpendicular to the surface. Because of the strong electric fields close to the ion when it is adsorbed on the surface, we should expect the conduction electrons in the metal to be drawn towards the ion so that the dipole moment should be considerably less than we would calculate for a caesium ion at a distance from an ideal metal surface equal to its radius. The experimental values of M have actually been found to be 16.2×10^{-18}, whereas we calculate 25×10^{-18} for a spherical caesium ion in contact with an ideal conducting plane.

The force f between two such adion dipoles is given by

$$f = (3/2)M^2/r^4, \tag{21}$$

where r is the distance between the adions.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

We may now work out the equation of state of the adsorbed caesium films in terms of these forces by means of Clausius' virial equation which for surfaces takes the form

$$F = \sigma kT + (1/4)\sigma \sum (rf), \tag{22}$$

where the summation is to extend over all adatoms which act on any one adatom. The forces f are of two kinds: first, the long range forces which correspond to the dipole repulsion given by Eq. (21), and second, the short range forces acting between atoms in contact which prevent any two from occupying a single elementary space at the same time. These short range forces may be taken into account by dividing the second member of Eq. (6) by $(1-\Theta)$, as has already been done in Eq. (7). In this way by an integration process it has been possible to derive the general equation of state for adsorbed atoms which repel as dipoles. This equation is

$$F = \sigma kT/(1-\Theta) + 3.34\sigma^{5/2}M^2 + 1.53 \times 10^{-5}\sigma^2 T^{1/3} M^{4/3} I, \tag{23}$$

where I is an integral whose numerical value can never exceed 0.89 and which can be obtained from tables and curves from the value of M, σ and σ_1.

The spreading force F calculated in this way cannot be measured directly for a solid surface but it can be related to the rate of evaporation ν_a by means of Gibbs' equation

$$\frac{dF}{d \ln \nu_a} = \sigma kT. \tag{24}$$

By substituting in this equation the values of F from Eq. (23), ν_a can be calculated in terms of M. Actually we have reversed the process. From the experimentally determined values of ν_a as functions of σ and T, we have calculated F by Eq. (24) and from these by Eq. (23) have obtained M. These values of M are found to be functions of σ but are not appreciably dependent on T, although a slight dependence is indicated by the form of Eq. (23).

A test of this theory can be made since the values of M obtained from ν_a may be compared with values of M obtained from the contact potential which may in turn be obtained from measurements of ν_e. The contact potential V of a surface covered with an adsorbed film as compared with that of a pure metal surface is given by

$$V = 2\pi\sigma M. \tag{25}$$

Furthermore the electron emission ν_e is related to the contact potential V by the Boltzmann equation

$$\nu_e/\nu_w = \exp\,(Ve/kT), \tag{26}$$

where ν_w is the electron emission from pure tungsten at the same temperature. The full line curve in Fig. 2 gives values of V calculated by Eq. (25) from M as determined from ν_a. The points shown by small circles represent values of V obtained from ν_a by Eq. (26).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The values of V obtained by these two independent methods agree nearly perfectly when $\theta < 0.5$. The deviations at higher values of θ seem to indicate that for high values of θ the short range forces are somewhat greater than those given by the factor $1-\theta$, the denominator of the first term of the second member of Eq. (23). Calculation shows that for a value of $\theta = 0.75$, that part of the spreading force which is due to the short range forces is actually 45 per cent greater than is given by the first term in the second member of Eq. (23).

It is also possible to calculate the contact potential from data on ν_p, the rate of evaporation of ions from the surface. The values of ν_a, ν_e and ν_p must be so related to one another that they give concentrations of atoms, electrons and ions in the vapor space near the filament which agree with the thermodynamical requirement for equilibrium among these particles. We may thus put

$$n_e n_p / n_a = K, \tag{27}$$

where K is the equilibrium constant that can be determined from the ionizing potential in accordance with the Saha equation. When this is done, and we combine with the Boltzmann equation and the Dushman equation for the electron emission from tungsten, we obtain

$$\ln(2\nu_p) = \ln \nu_a + (e/kT)(V_w - V_i - V), \tag{28}$$

where V_i is the ionizing potential of caesium, and V_w is the heat of evaporation of electrons from tungsten. The values of the contact potential V calculated from ν_p in this way are indicated in Fig. 2 by crosses. These points lie on the curve obtained from ν_a.

This agreement of the values of V obtained by these three methods shows that our theory gives a complete account of the electrical and chemical properties of moderately dilute adsorbed films of caesium on tungsten. It proves also that the surface of these tungsten filaments was essentially homogeneous, so that the probability of evaporation of any adatom or adion was independent of the position of the atoms on the surface and was determined wholly from the value of σ at that point.

The experiments showed, however, that this conclusion, although true for over 99 per cent of the surface, did not hold exactly. Deviations at very low values of θ indicated that about 0.5 per cent of the surface consisted of what we may call active spots which adsorbed caesium far more strongly than the rest of the surface, so that the heat of evaporation of these areas was about 37 per cent greater than that for atoms on the normal part of the surface. Experiments also showed that adsorption on this part of the surface was of the type indicated by Eq. (17): the simple type of adsorption sotherm. This means that the atoms adsorbed in the active areas did not exert appreciable forces on one another. Evidently the active spots consist of separated elementary spaces distributed over the surface, probably near grain boundaries or at steps in the crystal faces.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

A variation of the dipole moment M with σ results from the depolarizing effect of neighbouring dipoles. The electric fields due to these dipoles can be calculated by an integration process similar to that used in calculation of F, and are of the order of 5×10^7 volts cm^{-1}.

When a tungsten filament is heated to about 1100° in caesium vapor and there is an accelerating field drawing ions from its surface, two coexistent surface phases may occur. For one of these Θ is about 0.15, while in the other

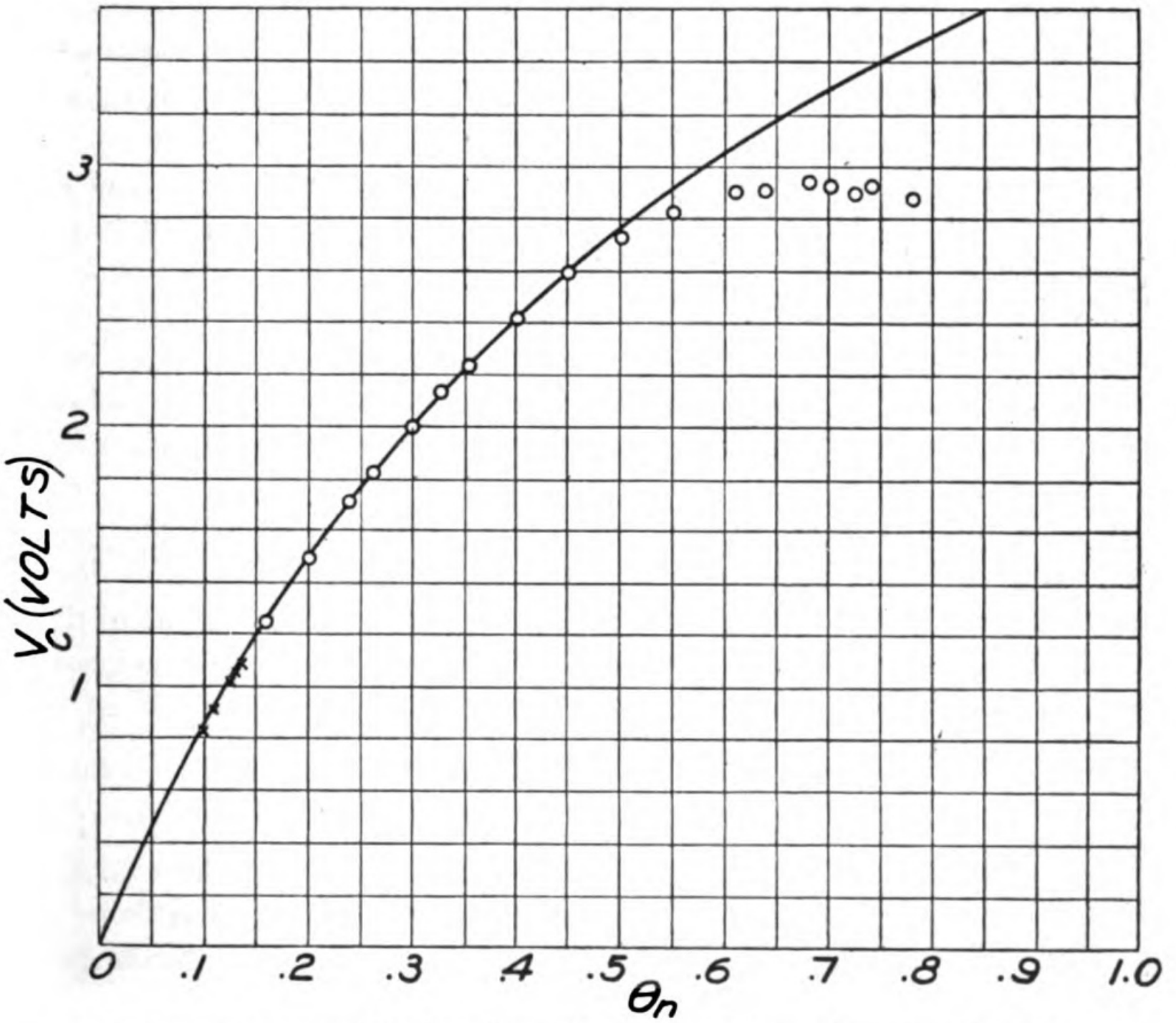


FIG. 2. Contact potential of caesium films on tungsten against clean tungsten.

it is very close to zero. The atoms that strike the less concentrated phase evaporate as ions, while those that strike the concentrated phase evaporate as atoms. The phase boundary is perfectly stable and stationary at a definite temperature in the presence of a given pressure of caesium. If the temperature is raised slightly, the phase boundary moves towards the concentrated phase, so that the whole filament gradually becomes bare; a lowering of the temperature causes the whole surface to become covered with the concentrated phase. A detailed analysis of the mechanism at the boundary between the phases which involves diffusion from one phase to the other, makes it possible to measure the surface diffusion coefficient D. Results have shown that

$$\log D = -0.70 - 3060/T.$$

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

From the temperature coefficient of D it can be calculated that the surface diffusion activation energy is about 0.6 volts. This means that between each of the elementary spaces there is a potential barrier of the height of 0.6 volts over which the adatoms must hop in order to migrate over the surface.

The experimental methods involved in these studies of caesium films on tungsten are capable of very great accuracy and sensitiveness, so that they seem to offer a rich field for the detailed study of adsorption phenomena. Dr. Taylor and I are continuing work in this field. We are planning to make accurate comparisons between the properties of films of adsorbed caesium, rubidium and potassium. We have developed a method of introducing definite small amounts of oxygen by diffusion through a heated silver tube. In this way known numbers of oxygen atoms may be placed on the surface of a tungsten filament thus forming negative dipoles. These attract the positive caesium dipoles which tend to form clusters around them, forming a kind of 2-dimensional colloidal distribution of caesium. We hope by the detailed study of such systems to learn the effects not only of repulsive but also of attractive forces between adatoms. Experiments are also in progress to study the adsorption of caesium on tungsten surfaces containing known numbers of adsorbed thorium atoms.

In such ways as these, together with the methods involving the spreading of oil films on water, it becomes possible to determine the equations of states of 2-dimensional gases, with nearly the same degree of accuracy as in the case of 3-dimensionals, but with the further advantage that the conditions are especially favorable for the determination of the mechanism of all of the processes involved.

Types of Adsorption

The classical kinetic theory of gases, as for example in the treatment of viscosity by Sutherland and of the continuity of the transition from gas to liquid by van der Waals, led to the recognition of attractive forces between molecules at large distances and of strong repulsive forces at short distances. The chemist has long known that exceptionally large attractive and repulsive forces are associated with the chemical union between adjacent atoms, which he represents by the valence bond (primary valence) and that weaker forces, which he has called secondary valence forces, usually correspond to other types of chemical combinations. The physicist has studied the forces between charged particles, such as ions and dipoles, and more recently has discovered the interchange forces, which are best explained in terms of quantum mechanics.

In the structure of matter there can be no fundamental distinction between chemical and physical forces: it has been customary to call a force *chemical*, when it is more familiar to chemists, and to call the same force *physical*, when the physicist discovers an explanation of it. There are also usually no sharp dividing lines between attractive and repulsive forces or between the various

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

kinds of attractive or repulsive forces. Nevertheless a recognition of various types of forces responsible for the stability of matter proves useful in classifying natural phenomena. Thus in a qualitative way we may consider the following types of forces (29):

(1) Coulomb forces between ions or ions and electrons varying with $1/r^2$ where r is the distance between ions. The best examples of these forces are in salt-like substances.

(2) Forces between dipoles which vary with $1/r^4$ and depend on the orientation of the dipole.

(3) Valence forces, associated with the sharing of electrons between atoms.

(4) Van der Waals' attractive forces, which depend on the mutual polarizability of molecules. These forces are usually considered to vary with $1/r^7$.

(5) Repulsive forces due to the mutual impenetrability of completed electronic shells. It is primarily these which determine the collision areas of molecules in the kinetic theory. Born and Mayer (33) find that the potential energy of these repulsive forces between two completed shells is given by

$$A \exp\left[(r_1+r_2-r)/r_0\right],$$

where r_1 and r_2 are the effective radii of the two shells and r_0 is a universal constant equal to 0.435 A°, while A is another universal constant. This means that this type of repulsive force between two atoms can be expressed as a function of the distances between the *surfaces of the atoms*, this function being the same for nearly all atoms (or molecules) which have completed shells, regardless of their electric charge. From a consideration of several of the other properties of solids and liquids I had previously drawn a similar conclusion (Ref. 20, pp. 529–531), that the repulsive forces should be regarded "'as surface forces which should be expressed as functions of the distances between the surfaces of the atoms (fixed by the electron orbits), rather than in terms of the distances between the centers of the atoms". A consideration of van der Waals' forces showed that for these also the "intensities of the fields around different non-polar molecules are practically identical when regarded as surface forces".

The fact that these repulsive forces, according to Born and Mayer, decrease to $1/e^{th}$ value for each increment of 0.435 A° in the distance between the atoms, indicates that they have a very small range of action.

(6) *Electron pressures.*—The force that counterbalances the Coulomb attraction of the electrons and ions in the alkali metals—and probably in other metals—is that due to the pressure of the Fermi electron gas.

Since all of these forces can be effective at the surface as well as in the interiors of solids and liquids, they must take part in adsorption phenomena. There should thus be various types of adsorption corresponding to the several types of forces which hold the atoms or molecules on the surface. Let us consider some examples:

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Caesium on Tungsten.—The caesium ions are held by Coulomb attractive forces (here a modified image force) to the underlying metal. The corresponding repulsive forces which hold the ion a definite distance from the surface (and thus determine the dipole moment M) result from the pressure gradient in the Fermi electron gas which extends beyond the lattice of tungsten atoms. The forces between the caesium adatoms are typical dipole repulsions.

Oxygen on Tungsten or Carbon.—The attractive forces are probably typical valence forces. That they are not ordinary Coulomb forces, such as those effective in caesium adsorption, is suggested by a consideration of the relation of the contact potential to the heat of evaporation of the adatoms. A film of caesium which has the maximum effect on the electron emission ($\theta = 0.67$) has a contact potential of $+3.0$ volts against tungsten, while the heat of evaporation of the adatoms corresponds to 1.9 electron volts. With an oxygen film produced when a tungsten filament at 1600° is in contact with oxygen at low pressure, the contact potential against tungsten at 1600° is -1.6 volts, but the heat of evaporation is about 7 volts.

The adsorption of oxygen, hydrogen and carbon monoxide on platinum (36) affords other examples of adsorption dependent on primary valence forces.

Oil Films on Water.—In these cases the attractive forces that cause the active heads to spread over the surface are principally dipole forces between the heads and the water molecules with some contribution from van der Waals' forces. Above the heads there is a hydrocarbon phase in which van der Waals' forces and the repulsive forces between completed shells predominate.

Non-Polar Gases on Glass.—The adsorption of such gases as nitrogen, argon, etc. on glass or mica at low temperatures is determined by typical van der Waals' forces (24).

Activated Adsorption

Because of the various types of adsorption that exist, a single gas may be adsorbed by a given surface in several different ways. At sufficiently low temperatures van der Waals' forces alone would be sufficient to cause adsorption (van der Waals' adsorption). At higher temperatures molecules on the surface may undergo chemical change and thus be held by valence forces. The heat of adsorption is then far greater than corresponds to the van der Waals' adsorption. The only reason that such adsorption does not occur at low temperatures is that the reaction velocity of the chemical change may be too low. Since there is an activation energy associated with each such reaction, H. S. Taylor (34) has proposed the term ***activated adsorption*** for the adsorption which involves such chemical changes.

In some cases, such as the adsorption of caesium atoms on tungsten, the adsorption involves only the transfer of one electron and can thus occur at very low temperatures so that activation is not required, and only one type of adsorption is observed.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The distinction between van der Waals' adsorption and activated adsorption was pointed out by the writer (Ref. 24, pp. 1399–1400) in 1918 and illustrated by the adsorption of carbon monoxide and of oxygen on platinum. At the temperature of liquid air and with a clean platinum surface in contact with carbon monoxide at a pressure of ·16 baryes, the surface concentration σ of the adsorbed carbon monoxide was 3.9×10^{14} molecules cm^{-2}, but, as the temperature of the platinum gradually rose to 20°C, σ *decreased* to 1.4×10^{14} and then *increased* again to 3.9×10^{14} and remained nearly constant until 200°C had been reached. When oxygen was brought into contact with platinum at liquid air temperature, 1.5×10^{14} molecules cm^{-2} were adsorbed immediately. On raising the temperature to 20°C, σ increased very slowly (in 18 hours) to 3.0×10^{14}. At 360°C σ rose to 4.8×10^{14}. It was concluded "that at liquid air temperature platinum adsorbs carbon monoxide in much the same way that glass does, that is, by secondary valence forces. With a moderate rise in temperature this gas is released, but in the neighborhood of room temperature the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film."

In a discussion of the mechanism of the dissociation of hydrogen on tungsten filaments in 1916 the writer considered (7) the possibility that the adsorbed hydrogen exists on the surface in two forms and that the velocity of interaction between these forms may determine the rate of production of atomic hydrogen. The mathematical formulation which was given is applicable to many cases of activated adsorption.

Within recent years H. S. Taylor (34) and his co-workers have discovered many cases of activated adsorption and have demonstrated their importance in an understanding of contact catalysis. The velocity of the activation reaction, which is often low even at a temperature of several hundred degrees, has been measured and the activation energy calculated. Other investigators have sought to explain these slow surface reactions by assuming solution of the adsorbed gas in the underlying substance or slow penetration into cracks or capillary spaces.

That this cannot be a general explanation is proved by some experiments (35) that Dr. Blodgett and I have made on the thermal accommodation coefficient of hydrogen in contact with tungsten. At temperatures from 200°K to 600°K a stable adsorbed film of hydrogen on tungsten is formed which gives an accommodation coefficient α of about 0.22. As the temperature is raised, this film goes over slowly into a much more stable film which is characterized by a value of $\alpha = 0.14$. The reaction velocity is such that the formation of the stable film requires several minutes at 600°K and a small fraction of a second at 900°, indicating an activation energy of the order of at least 20 Kg calories per molecule. Since the accommodation coefficient is a purely surface property, these experiments prove that these two forms of hydrogen film are both monatomic films which probably represent two kinds of chemical binding

Digitized by Google Original from UNIVERSITY OF MICHIGAN

by valence forces. At temperatures below liquid air temperature a clean tungsten surface would undoubtedly show also van der Waals' adsorption of hydrogen. This would thus be a third kind of adsorbed film of hydrogen on tungsten.

Catalytic Action of Surfaces.—A monatomic film of oxygen on tungsten at 1500° acts as a catalytic poison for nearly all the reactions which would otherwise occur in contact with the tungsten surface (15). Thus the dissociation of hydrogen into atoms at 1500°K is stopped by a trace of oxygen, as is also the decomposition of ammonia, methane or cyanogen. The effect of the oxygen is to cover the surface so that the other gas cannot make contact with the tungsten surface.

Similarly hydrogen and carbon monoxide act as catalytic poisons on platinum surfaces (36). The rate at which carbon monoxide and oxygen combine in contact with platinum is proportional to the pressure of oxygen and inversely proportional to the pressure of the monoxide. The reaction velocity depends on that fraction of the platinum surface which is *not covered* by adsorbed molecules of carbon monoxide. The oxygen molecules that can become adsorbed in these vacant spots and so be adsorbed on the platinum surface can thus react with adjacent adsorbed molecules of carbon monoxide.

In numerous cases investigated, the action of a surface in catalyzing a gas reaction involves just such interaction between molecules adsorbed in adjacent elementary spaces on the surface. On this basis it is possible to develop (7) (13) (36) a "law of mass action" for the velocity of surface reactions by which the observed reaction velocities can be explained quantitatively. It has been pointed out (15) that reactions of this sort are extremely sensitive to the actual distances between the atoms in the surface of the catalyst. Thus with many surfaces there is only a relatively small fraction of the surface on which the reaction can occur with extreme rapidity, while over the larger part of the surface it takes place at a negligible rate. A quantum theory explanation of the importance of the spacing of the atoms in the catalyst has recently been given by Sherman and Eyring (37).

The presence of a second layer of adsorbed atoms or molecules, although this second layer may cover only a minute fraction of the surface, is often of great importance in the mechanism of gas reactions brought about by a surface catalyst.

Thus in the oxidation of heated tungsten filaments in oxygen at low pressures by which WO_3 is formed, the oxygen molecules incident on a surface already nearly completely covered by a monatomic film of oxygen atoms, condense and momentarily exist in a second adsorbed layer (Ref. 29, p. 473). Although the rate of evaporation from this second layer is so high that the surface concentration is very low, the adsorbed atoms or molecules in this layer move freely over the surface and thus fill up the holes in the first layer,

Digitized by Google Original from UNIVERSITY OF MICHIGAN

formed when WO_3 molecules evaporate, far faster than would otherwise be possible. These atoms in the second layer can also interact with those in the first layer and with the underlying tungsten to form the molecules of WO_3 which escape from the surface.

List of References

(The papers are by I. Langmuir except as indicated.)

1. *Indust. Eng Chem.*, **20**, 332 (1928). This paper gives an account of the author's early work on gases in lamps.
2. *J. Am. Chem. Soc.* **37**, 1139–1167 (1915). "Chemical Reactions at Low Pressures."
3. *J. Am. Chem. Soc.* **34**, 1310–25 (1912). "A Chemically Active Modification of Hydrogen."
4. *J. Am. Chem. Soc.* **34**, 860–77 (1912). "The Dissociation of Hydrogen into Atoms."
5. I. LANGMUIR and G. M. J. MACKAY, *J. Am. Chem. Soc.* **36**, 1708–22 (1914).
6. *J. Am. Chem. Soc.* **37**, 417–58 (1915).
7. *J. Am. Chem. Soc.* **38**, 1145–56 (1916).

These three papers describe determinations of the degree of dissociation of hydrogen at high temperatures.

8. *Gen. Elect. Rev.* **29**, 153 (1926). "Flames of Atomic Hydrogen" and a recalculation of the degree of dissociation.
9. *Trans. Am. Electrochem. Soc.* **29**, 294–5 (1916); also Gen. Electric Rev. **16**, 962 (1913).
10. A. E. FREEMAN, *J. Am. Chem. Soc.* **35**, 927 (1913).
11. *J. Am. Chem. Soc.* **35**, 105 (1913). "The Clean-Up of Oxygen in a Tungsten Lamp."
12. I. LANGMUIR and D. S. VILLARS, *J. Am. Chem. Soc.* **53**, 495 (1931).
13. *J. Am. Chem. Soc.* **38**, 2221–2295 (1916). "Constitution and Fundamental Properties of Solids and Liquids." Part I.
14. *Trans. Electrochem. Soc.* **29**, 262 (1916).
15. *Trans. Faraday Soc.* **17**, 607 (1921). "Chemical Reactions on Surfaces."
16. *Phys. Rev.* **22**, 357 (1923). "Electron Emission from Thoriated Tungsten Filaments."
17. *Met. Chem. Eng.* **15**, 468 (1916).
18. *J. Am. Chem. Soc.* **39**, 1848–1906 (1917). "Constitution and Fundamental Properties of Solids and Liquids." Part II.
19. I. LANGMUIR, Third Colloid Symposium Monograph (1925) p. 48 (Chemical Catalog Co., N.Y.). "The Distribution and Orientation of Molecules."
20. Article by LANGMUIR entitled "The Effects of Molecular Dissymmetry on Properties of Matter" in Jerome Alexander's book: *Colloid Chemistry*, Vol. 1 (1926) p. 525–546.
21. *Proc. Natl. Acad. Sciences* **3**, 251–7 (1917). "The Shapes of Molecules Forming the Surfaces of Liquids."
22. A series of papers by N. K. ADAM in *Proc. Roy. Soc.* (*London*). See book: *Physics and Chemistry of Surfaces*, N. K. ADAM. Clarendon Press, Oxford, 1930.
23. J. TRAUBE, *Ann. d. Phys.* **265**, 27–55 (1891).
24. *J. Am. Chem. Soc.* **40**, 1361–1403 (1918). "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum."
25. *Phys. Rev.* **40**, 463 (1932). "The Mobility of Caesium Atoms Adsorbed on Tungsten."
26. *Phys. Rev.* **8**, 149–176 (1916). "Evaporation, Condensation and Adsorption."
27. *Proc. Natl. Acad. Sciences* **3**, 141–7 (1917). "The Condensation and Evaporation of Gas Molecules."
28. *J. Am. Chem. Soc.* **54**, 2798 (1932). "Vapor Pressures, Evaporation, Condensation and Adsorption."
29. *Chem. Reviews* **6**, 451–77, (1929). "Forces Near the Surfaces of Molecules."

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

30. "The Rates of Evaporation of Atoms, Ions and Electrons from Caesium Films on Tungsten," a paper by LANGMUIR and J. B. TAYLOR soon to appear in *Phys. Rev.*

31. *Science* **57**, 58 (1923).

32. LANGMUIR and K. H. KINGDON, *Proc. Roy. Soc.* (A) **107**, 61 (1925). "Thermionic Effects Caused by Vapors of Alkali Metals."

33. M. BORN and J. E. MAYER, *Z. Physik* **75**, 1 (1932).

34. H. S. TAYLOR, *J. Amer. Chem. Soc.* **53**, 578 (1931).

35. K. B. BLODGETT and I. LANGMUIR, *Phys. Rev.* **40**, 78–104 (1932). "Accommodation Coefficients and Surface Films."

36. *Trans. Faraday Soc.* **17**, 621 (1921). "Catalytic Oxidation of Hydrogen and Carbon Monoxide by Platinum."

37. A. SHERMAN and HENRY EYRING, *J. Amer. Chem. Soc.* **54**, 2661–75 (1932). "Quantum Mechanics of Activated Adsorption."

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

SURFACE CHEMISTRY

THE DENKI-GAKKWAI

CHEMISTS have long been familiar with the phenomenon of adsorption which is the condensation of dissolved or gaseous substances on a surface. The surface may be the boundary between any two phases. It may, for example, be at the interface between two liquids which do not mix. When Sir James Dewar found that charcoal, cooled to the temperature of liquid air, was capable of taking up large quantities of such gases as oxygen and nitrogen, it was explained that these gases were condensed upon the surface of the charcoal. The very fine state of division of the charcoal which should give it an enormous surface thus accounted for the large amount of gases adsorbed under these conditions. An example of adsorption with which everyone is familiar is that of the action of soap on water. Water is a liquid that possesses an unusually high surface tension. If a finger is dipped into clean water, the drop that hangs from the finger on removing it from the water is much larger than it would be in the case of any other ordinary liquid. The force that holds the drop of water against the force of gravity is the surface tension. It amounts to about 73 dynes per centimeter which acts across any part of the free surface of the water.

If the merest trace of soap be dissolved in water, the surface tension of the water is greatly lowered by 20 dynes per cm or more. This naturally results in smaller drops being formed. Anyone may demonstrate this effect to himself by merely dipping a finger of one hand into a glass of clean water and a finger of the other hand into a glass of soapy water. It will be seen that when the fingers are withdrawn the drops of pure water are several times larger than those of soapy water.

Willard Gibbs showed by theoretical reasoning that any substance which lowers the surface tension of a liquid always does so by being concentrated into the surface layer, or, in other words, by being adsorbed at the surface of the liquid. An equation that Gibbs derived may readily be put in the form

$$\frac{dF}{d(\log_e p)} = \sigma kT \qquad (1)$$

where p is the partial pressure of the vapor of the adsorbed substance in equi-

---

[EDITOR'S NOTE: This material was presented as a lecture in Japan under the auspices of the Institute of Electrical Engineers of Japan, and printed in *The Denki-Gakkwai*, Nov., 1934.]

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

librium with the surface, σ is the number of molecules adsorbed on the surface per unit area, T is the absolute temperature, k is the Boltzmann constant 1.37×10^{-16} erg. per deg., and F, which may be called the spreading force, is given by

$$F = \gamma_0 - \gamma \tag{2}$$

where γ_0 is the surface tension of the pure solvent and γ is the surface tension of the solution.

Early Theories of Adsorption

Prior to 1910 many different theories of adsorption had been proposed, but none of them had been very successful. In most of these theories the increased concentration of the adsorbed substance near the surface was thought to be analogous to the retention of the earth's atmosphere by the gravitational attraction of the earth. An adsorbed gas was thus regarded as a kind of miniature atmosphere extending out a short distance from a solid substance. In general, such theories were called upon to account only for qualitative aspects of the adsorption of gases on solids. Most of the knowledge of adsorption was empirical. Even Gibbs' law had not been verified experimentally.

Formation of the Atomic-hydrogen Layer

In a previous article[1] I told you how I was led to believe that the hydrogen atoms, which were produced when a tungsten filament was heated in a bulb containing a trace of hydrogen, formed on the inner surface of the glass bulb a film which never exceeded in thickness that of a single hydrogen atom. This conclusion regarding the thickness of the film was suggested by the properties of atomic hydrogen, for hydrogen atoms should combine so readily to form molecules that a double layer of hydrogen atoms could never be formed.

This picture of the film of adsorbed hydrogen atoms on a glass surface was very different from a miniature atmosphere extending out some distance from the solid surface, and I began to wonder whether there were not other cases besides that of atomic hydrogen where atoms or molecules could be held on surfaces by direct chemical action, or chemical combination, with the surface.

The experiments which I made in studying the effect of various gases in a bulb with a tungsten filament soon furnished me with a still more striking example of a stable chemically adsorbed film on a solid. When a tungsten

---

[1] "Fundamental Industrial Research", by Dr. Irving Langmuir *General Electric Review*, vol. 38, No. 7, July 1935, pp. 324–333.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

filament is heated to about 1500 deg. K in oxygen at very low pressures, such as 0.1 mm or less, the oxygen reacts chemically with the tungsten to form the oxide WO_3 which evaporates from the filament at this temperature as fast as it is produced, leaving the surface of the filament apparently clean. There are many facts, however, that prove that the surface of the filament has been modified by the admission of the oxygen. For example, the electron emission from the filament at 1500 deg. K has been reduced to about 1/100,000th of that which could have been observed before the oxygen was admitted. The oxygen soon disappeared completely from the bulb as it was used up by the oxidation of the tungsten, but the electron emission stayed indefinitely at this low value even after the oxygen was gone. It seemed that such a behavior might be produced by the presence of a very stable adsorbed film of oxygen on the surface of the tungsten filament. In view of the experimental results, it was necessary to assume that this film did not evaporate appreciably even into a perfect vacuum during many hours at 1500 deg.

Once having produced this film on the surface of the tungsten, it was interesting to find out whether at higher temperatures it could be made to evaporate. Heating the filament for about a half hour at 1860 deg., or about 20 seconds at 2007 deg. was sufficient to make the electron emission at 1500 deg. increase more than 100-fold.

The chemist has found that the rate at which evaporation increases with the temperature can be used to calculate the latent heat of evaporation. The temperature coefficient of the evaporation of these oxygen films on tungsten is enormously high, the rate being increased 100-fold by raising the temperature about 200 deg. From this it may be calculated that the heat of evaporation of the film on the tungsten is 162 kg-cal. per gram atom, which is a far greater amount of energy than corresponds to the heat of combustion of hydrogen in oxygen. This means that this oxygen film is held on the surface of the tungsten by forces much greater than those involved in the formation of ordinary stable chemical compounds. It seemed, therefore, that one should regard the oxygen atoms as being combined directly with the underlying tungsten atoms of the surface. If this is so, one would hardly expect that a second layer of oxygen atoms should form on the surface, for the atoms in the second layer could only combine chemically with the first layer of oxygen atoms, and from the properties of oxygen we would not expect oxygen atoms to combine firmly with other oxygen atoms which are already chemically saturated.

I have already told you how the heated tungsten filament dissociates hydrogen molecules and thus, because of the adsorption of the hydrogen atoms on the glass, causes a disappearance or clean-up of the hydrogen. A minute trace of oxygen, enough to give a pressure of only about 10^{-6} mm is sufficient to prevent completely this dissociation of hydrogen into atoms by a tungsten

Digitized by Google Original from UNIVERSITY OF MICHIGAN

filament at 1500 deg., apparently by merely keeping the hydrogen from making contact with the tungsten. Very interesting results are obtained if a mixture of oxygen and hydrogen at low pressure is brought into a bulb containing a tungsten filament at 1500 deg. Because of the presence of the oxygen the hydrogen does not dissociate, but the hydrogen does not prevent the oxygen from behaving in a normal way toward the tungsten filament. Thus, the oxygen gradually disappears by reacting with the tungsten filament until after about 20 min the pressure has fallen to about 10^{-6} mm, and then the hydrogen suddenly begins to dissociate and thereafter continues at the same rate as though no oxygen had been present. The action of oxygen on this reaction is like that of a poison; in fact the chemist calls a substance that stops a chemical action in this way a catalytic poison.

The fact that the monatomic film of oxygen on tungsten does not react with hydrogen at 1500 deg. is a striking indication that the oxygen in the adsorbed film has properties very different from that of ordinary gaseous oxygen. This change in properties, however, should not surprise us if we look upon the oxygen on the surface as being chemically combined with the tungsten. For example, the oxygen in calcium oxide does not react with hydrogen at 1500 deg. Judging from the temperature coefficient found in the experiments at higher temperatures, we may conclude that an oxygen film on tungsten at 1500 deg, should take more than a year to evaporate. It is thus remarkable that the hydrogen clean-up begins so suddenly, and within a few minutes after starting all of the hydrogen has disappeared by dissociation. This proves that the hydrogen, after it begins to reach the tungsten surface, can remove all of the oxygen on the surface very quickly. If the oxygen atoms are packed tightly side by side in a surface lattice, the hydrogen cannot release them from the tungsten surface, but if there are enough vacant spaces on the surface so that a few hydrogen atoms can be adsorbed, they appear to be able to react directly with oxygen atoms which are adsorbed in adjacent spaces.

New Theory of Adsorption

Experiments of this sort led to a theory of adsorption which was very different from those that had been prevalent up to that time. According to the new theory the surface of a tungsten filament is to be regarded as a surface lattice or checkerboard which can hold adsorbed atoms in definite positions. The forces involved are those acting directly between the adsorbed atoms and the atoms of the underlying metal. If a second layer of atoms could be formed on top of the first, the forces holding these atoms would then be quite different from those that hold the atoms in the first layer. In other words, the structure of an adsorbed film is considered from somewhat the same point of view as that of the organic chemist when he derives the structure of the molecules of organic substances.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The older views on adsorption are now often referred to as constituting a physical theory of adsorption, whereas the newer ideas are described as a chemical theory I think this distinction involves not so much the nature of the forces involved in adsorption as the traditional attitude of mind of physicists and chemists. The physicist, probably ever since the time of Newton, has been inclined to consider forces which vary as some power of the distance between the bodies acted upon by the forces. He has also had many occasions to consider fields of force which extend throughout space, such as gravitational, electric, and magnetic fields. The chemist, on the other hand, has nearly always considered that chemical action between molecules or atoms takes place only when they are in contact. It is a natural tendency for the physicist in considering the problem of adsorption to think of the behavior of the adsorbed atoms or molecules as being in a field of force produced by a solid or liquid surface. It would be more in accord with the tradition of the chemist, however, to think of an atom on the surface as being attached to one or more atoms of the underlying surface.

In very recent years this distinction between the attitudes of physicists and chemists is fast disappearing, for the physicist has become convinced that the great majority of the forces involved in the structure of matter have such a short range of action that the forces become practically negligible unless the atoms from which they originate are nearly in contact. The difference between physical and chemical theories is thus becoming of merely historical interest. It should, however, be emphasized that the older methods of the chemists by which he derived the structure of chemical compounds should be looked upon more favorably than ever, and that they now receive support and justification from modern physical theory. The simple, chemical pictures of phenomena are particularly well suited to those who wish to consider such problems as adsorption from the practical point of view rather than to go into elaborate mathematical calculations for which adequate data are rarely available.

Forces Between Atoms

Except where we have to deal with electrically charged atoms or molecules, or with electric dipoles of large magnitude, the forces between atoms or molecules decrease so rapidly with increasing distance between the particles that when the surfaces of the atoms or molecules are separated by as much as 10^{-8} cm the forces become relatively insignificant compared with those that exist when the particles are in contact. A mere recognition of this fact of the short ranges of the forces usually involved in adsorption is sufficient to serve as the basis for a theory of adsorption which is in much better agreement with general observation than any theory which would have been derived by the traditional methods of the physicists.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

Most recent experimental studies of adsorption have shown that there is a strong tendency for the adsorbed film to be one atom or molecule in thickness. A simple analysis taking into account the short range of the forces makes it clear why this tendency should exist and also indicates to us under what conditions thicker films can be formed. It is instructive to consider in this connection the equilibrium between a gas and a solid surface. The mechanism of the adsorption may be then considered in the following way:

The molecules in the gas are moving in all directions with kinetic energies that are determined by the temperature so that they come into contact with the solid at a definite rate, μ, which may be expressed as the number of molecules which strike the surface per unit area per unit time. The kinetic theory of gases enables us to calculate μ by the equation,

$$\mu = \frac{p}{(2\pi mkT)^{1/2}} \tag{3}$$

where m is the mass of the molecule. Inserting numerical values this equation becomes

$$\mu = 2.65 \times 10^{19} p (MT)^{-1/2} \tag{4}$$

where M is the molecular weight of the gas.

Inelastic Collisions of Molecules Striking Surfaces

In the kinetic theory of gases the collisions between molecules are usually considered to be perfectly elastic. At present the justification of this hypothesis is seen to lie in the fact that there is no mechanism by which two isolated molecules in space which come into contact at low velocities can lose any of their energy. When a molecule, however, strikes a solid surface, there is no reason to anticipate that energy cannot be given up readily to the surface. Recent experimental evidence by large numbers of observers indicates, in fact, that, in general, such collisions are inelastic. We may consider, therefore, in most cases that the incident molecule condenses on the surface and does not rebound elastically from it. If the temperature of the surface is sufficiently high, the condensed molecule can evaporate from the surface, the rate of evaporation depending not only on the temperature but on the magnitude of the forces of the attraction between the molecule and the solid. This relation may be expressed by the equation

$$\nu = A\epsilon^{-w/kT} \tag{5}$$

where ν is the rate of evaporation expressed in atoms per square centimeter per second, w is the heat of evaporation per atom, and A is a constant which is independent of the temperature If the heat of evaporation is large, the rate of evaporation increases extremely rapidly with increasing temperature.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Evaporation of Atoms

According to this theory the condensation and the evaporation processes are entirely independent of one another; that is, the probability that a given adsorbed atom will evaporate in any short time interval is independent of the time that has already elapsed since its condensation on the surface. Under these conditions the adsorbed molecules on the surface have a certain average life which is quite analogous to the life of a radioactive atom. If we divide the rate of evaporation, ν, by σ, the number of adsorbed atoms per square centimeter, we obtain the average probability per second for the evaporation of the individual atoms. The reciprocal of this, τ, is thus the average life of an adsorbed atom on the surface We thus have

$$\tau = \sigma/\nu \qquad (6)$$

This time lag that exists between the condensation and evaporation of the atoms on the surface may thus be looked upon as a fundamental cause of the adsorption of gases on solid surfaces.

The rates of evaporation of different substances in vacuum not only vary greatly with temperature in accordance with Equation (5), but also have an enormously wide range of values depending on the nature of the evaporating substance. When we consider that helium boils at 4 deg. absolute and tungsten at over 5000 deg, we must recognize the magnitude of this range.

If we consider the adsorption of such gases as helium, for example, on tungsten, the value of w is extremely small so that the exponent of Equation (5) is nearly zero. Under such conditions the life τ of the atoms on the surface may become of the order of magnitude of 10^{-13} sec, which is about the duration of the collision that the atom makes with the surface. Under these conditions there is no real distinction in time between condensation and evaporation, and the duration of the whole process may be so short that the atoms do not even have time to reach thermal equilibrium with the surface before they leave it. This phenomenon has been observed when gases of low boiling points strike filaments which are at relatively high temperature. For example, it is found that the accommodation coefficient of helium on tungsten may be as low as 0.1. This means that helium evaporates even before its adjustment of temperature has gone one-tenth of the way to thermal equilibrium. These are, however, rather unusual cases which correspond to small values of τ and do not indicate that the collisions between a gas and a solid are normally elastic.

When a solid surface is in equilibrium with a gas, the rates of condensation and of evaporation must become equal so that $\mu = \nu$, and then σ, the total amount adsorbed can be found according to Equation (6) to be

$$\sigma = \mu\tau \qquad (7)$$

Digitized by Google Original from UNIVERSITY OF MICHIGAN

If the atoms on the surface evaporate entirely independently of one another so that τ is not influenced by the number of atoms on the surface, then the amount adsorbed should increase proportionally to the pressure of the gas. However, it is clear that this cannot go on indefinitely, for if the number of adsorbed atoms becomes so great that they practically cover the surface, additional molecules which strike the surface from the gas are not able immediately to find vacant spaces in the first layer that they can occupy so that they must condense into a second layer. But these atoms are no longer in direct contact with the atoms of the underlying solid. The forces that hold them and which therefore determine the magnitude of w will, in general, be quite different from those that act upon the atoms that condense in the first layer. Therefore τ in Equation (7) depends upon σ, and we can no longer say that σ must increase in proportion to the pressure.

Life of an Atom in the Second Layer

Because of the short range of the forces that act on adsorbed atoms, we must recognize that the life τ of an atom in the second layer will be very different from that of the life of a similar atom in the first layer, since in these two cases the adsorbed atom makes contact with atoms of entirely different character. In general, we cannot say that the forces acting on atoms in the second layer will be less than those acting on the atoms in the first layer. We may merely say that they will, usually, be widely different. Let us consider, then, two cases:

First, suppose that atoms in the second layer are held by much weaker forces than those acting on atoms in the first layer. Then the average life τ_2 of the atoms in the second layer will usually be extremely small compared to τ_1, the life of the atoms in the first layer, since the effect of a change in the forces holding the atoms is to alter the exponent of Equation (5), and a small change in w produces a relatively great change in ν and in τ. Because τ_2/τ_1 is so small in this case, we can see by Equation (7) that σ_2/σ_1 will be equally small; in other words, there will be no appreciable adsorption in the second layer.

Let us now consider the second case, that the forces holding atoms in the second layer are greater than those acting on the first layer of atoms. An example of this kind has been found experimentally in the case of mercury or cadmium atoms which are allowed to strike upon a glass surface cooled to, say, -50 deg. C. These atoms have a much greater affinity for one another than they have for glass. The cadmium atoms in a second layer, being in contact with other cadmium atoms, evaporate much more slowly than do single atoms in the first layer. Under these conditions the temperature of the glass has to be lowered far below the temperature corresponding to saturated vapor before any appreciable number of atoms are present in

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the first layer. If the pressure is then raised sufficiently, these atoms in the first layer begin to form clusters which readily become covered by a second layer since the second layer is relatively so stable; the third, fourth, and subsequent layers thus begin to form on these nuclei even before the first layer is complete. This leads to the formation of small detached crystals. There is nothing abnormal about this kind of condensation on solid surfaces. It is typical of the cases where the forces between adsorbed atoms are greater than those between these atoms and the underlying surface. These cases, however, do not give us the typical phenomenon of adsorption. It is just because the formation of uniform layers of adsorbed molecules requires that the forces between the adsorbed molecules shall be less than those exerted by the underlying surface that adsorbed films are only rarely more than one molecule in thickness.

Films of Thorium on Tungsten

The marked effect of a monatomic film in modifying the electrical properties of a metal surface may be illustrated by films of thorium on tungsten. This effect was discovered in 1913 in connection with the work done in studying the possibility of obtaining electron emission from a metal in the highest possible vacuum, which I described in an earlier article.[1] I have told you that the general consensus of opinion seemed to be that the electron emission became very small as the vacuum was improved and might perhaps disappear entirely in a perfect vacuum. I found that the difficulties that others had experienced in studying these phenomena arose from their having overlooked the space-charge effect and I therefore attempted to measure the electron emission from tungsten in a vacuum so good that residual gas could have no effect. For this purpose I mounted two supposedly pure tungsten filaments in a glass bulb and sealed two platinum wires through the surface of the bulb in such a way that they lay flat on the inner surface of the glass. Thus by vaporizing tungsten from one of these filaments in high vacuum, a metallic deposit was formed on the inner surface of the bulb giving conductivity between the two platinum wires. This deposit was used as the anode in measuring the electron emission from one of the filaments. I decided upon this kind of an anode, first because it would be free from gas, and secondly because I had found that the vaporization of tungsten from a filament at very high temperature caused a clean-up of residual gases to an extent far greater than could be obtained in any other way known at that time. During the exhaust of the bulb it was heated to the softening point of the glass and exhausted as well as possible. To make the vacuum still more nearly perfect and to avoid possible evolution of gases from the glass, the whole bulb was immersed in liquid air during the measurements.

With this procedure it gradually became possible to observe electron emission from the tungsten filaments at temperatures far lower than had been

Digitized by Google Original from UNIVERSITY OF MICHIGAN

needed during preliminary experiments in which such great precautions to produce good vacuum had not been taken. This seemed to indicate that instead of the electron emission being less in a very high vacuum it became much greater, but the results were erratic.

The Thoriated-tungsten Filament

In this work several tubes were made up and tested. Finally one tube was obtained which behaved entirely differently from the others in that no increase in the emission was produced by the refinements in the methods of producing high vacuum. This suggested that the difference might be caused by the use of other samples of tungsten. It was then discovered that, through a mistake, a thoriated-tungsten filament (that is, one made by the Coolidge process in which off-setting had been prevented by the addition of 0.5 per cent thorium oxide) had been used in making the first tubes in which this exceptionally high vacuum was produced. Further work soon showed that the abnormally high emission depended upon the presence of thorium in the filament and that the need for the unusually high vacuum in these experiments was merely to prevent the oxidation of the thorium.

When a bulb is made up with a thoriated filament, using another filament as anode instead of the vaporized deposit on the bulb, and the bulb is kept at room temperature, there is usually no evidence that the electron emission is any greater than that of a pure tungsten filament. By the better methods of producing high vacuum, and by a heat treatment of the thoriated filament which we had accidentally stumbled upon, it became possible to increase the electron emission of the thoriated filament at 1500 deg. K to a value about 100,000 times that from a pure tungsten filament of the same temperature. Without going further into the history of the development of the thoriated filament as a source of electrons in electrical discharges, let me describe the effects produced by thorium in terms of our present knowledge.

The best procedure for obtaining the monatomic film of thorium on the surface of a tungsten filament is to heat the filament, after the bulb has been well exhausted, to a series of increasing temperatures starting at about 2000 deg., finally heating the filament for about 30 sec to about 3000 deg. K. By this gradual heating of the filament a finely crystalline structure is obtained. The final heating at 3000 deg. reduces a portion of the thorium oxide to metallic thorium which remains distributed through the filament in solid solution.

At such a high temperature as 3000 deg. thorium oxide has a slight tendency to dissociate into thorium atoms and oxygen atoms. These oxygen atoms, however, diffuse out through the filament far faster than does the thorium, and thus near the surface of the filament the concentration of the atoms of oxygen becomes very small. This displaces the equilibrium between the thorium

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

and the oxygen so as to cause a great increase in the concentration of the metallic thorium near the surface of the filament. Even minute traces of oxygen or water vapor given off by the bulb in quantities too small to cause appreciable oxidation of the tungsten filament may still be sufficient to prevent this liberation of metallic thorium within the filament and so prevent the characteristic increase in electron emission of a thoriated filament.

By the procedure that I have described there is stored up just below the surface of the filament a supply of metallic thorium, but at high temperatures this thorium evaporates from the surface of the filament as fast as it arrives there by diffusion from the interior. Thus at 2400 deg., which is the temperature at which pure tungsten filaments are normally heated for use as a source of electrons, the emission of the thoriated filament is no greater than that of the pure tungsten filament.

An important step, therefore, in the production of a thoriated-tungsten cathode consists in heating the filament for a considerable time at a lower temperature, which we may call the activating temperature, at which thorium can still diffuse at a perceptible rate to the surface, but at a rate far greater than that at which it evaporates. The temperature coefficient of the evaporation is much greater than that of the diffusion and thus in the neighborhood of 2100 deg. the evaporation becomes negligible compared to diffusion. If the filament is held at an activating temperature of 2100 deg., the thorium gradually accumulates at the surface as a monatomic film. At this temperature, however, although the loss of thorium by evaporation is slow, it is still sufficiently great so that most of the available stored supply of metallic thorium that was produced at 3000 deg. would be lost in the course of a few hours.

It has therefore been found best during the life of the filament to maintain it at an operating temperature of about 1900 deg. at which the available thorium supply may last for thousands of hours. Under these conditions electron emissions of over 0.5 amp. per sq. cm can be obtained which is about as great as would be obtained from tungsten at 2500 deg. K. The energy necessary to heat the thoriated filament to get any given electron emission is less than one-third of that needed for pure tungsten.

Many millions of radio tubes have been made with these thoriated-tungsten cathodes. Within recent years oxide-coated cathodes, usually using barium oxide, have displaced the thoriated cathodes for receiving tubes, for they have a still greater efficiency than the thoriated cathodes. But for power tubes for industrial purposes and for radio broadcasting stations, the thoriated cathodes are still extensively used for they are far less sensitive to the harmful effects of the bombardment of the cathodes by positive ions from residual gas gas at the high voltages used in these tubes. The thoriated-tungsten cathode, therefore, may be regarded as the first industrial application involving the deliberate production of monatomic films on metals.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The extensive studies that have been made of the properties of thoriated tungsten filaments have made it possible to obtain intimate knowledge of such phenomena as the diffusion of thorium atoms through tungsten, the effect of adsorbed atoms on the electron emission, and the rate of evaporation of the adsorbed atoms as a function of temperature and of the concentration σ of the adsorbed atoms. We shall see later that even more detailed knowledge of phenomena of this kind may be obtained by the study of adsorbed caesium atoms on tungsten.

Monomolecular Films on Water

My purpose in delaying the further consideration of these adsorbed films on metal is that I would like first to discuss an entirely different set of experimental facts which throw a new light upon the structure of adsorbed films. I refer to monomolecular films on the surface of water. Interest in these phenomena was first aroused by the work of Lord Rayleigh and Miss Pockels about 1890. Lord Rayleigh pointed out that the properties of certain oil films on water could best be explained by assuming that they consisted of a single layer of molecules. Devaux and Marcellin, between 1903 and 1914, devised some beautiful, yet simple, experimental methods for measuring the thicknesses of oil films, and considered that this thickness gave the diameter of the molecules. In reading of this work I became interested in these monomolecular films because of the close analogy to the monatomic films on solids. I thought that a further study of these insoluble oil films should throw light upon the nature of the forces involved.

It was known that some oils spread on the surface of water while others do not, but no adequate reason had been given for this difference. It seemed also that since the amount of oil on the surface as well as the change in surface tension could be measured, there was an opportunity for using the Gibbs' equation in order to study the thermodynamic properties of these films.

When a drop of a so-called pure mineral oil, or a pure saturated hydrocarbon, is placed upon water, it floats on the water as a circular lens having a definite circular boundary where the oil, water, and air meet.

If we imagine an oil lens of this sort to be constrained by some force to spread out to a very thin film over the surface of the water, we can readily analyze the conditions that must be fulfilled in order that an oil can form such lenses on the surface of water. Outside of the lens there is the surface tension, γ_1, of the pure water. Within the boundary of the lens there are two surfaces — the oil-air interface and the oil-water interface — which have the surface tensions γ_2 and γ_{12}, respectively. In order that the thin lens may be stable, it is evidently necessary that γ_1 shall be equal to $\gamma_2+\gamma_{12}$. If these forces are not equal, the lens will either spread out indefinitely or will contract into a lens of such thick-

Digitized by Google Original from UNIVERSITY OF MICHIGAN

ness that gravitational forces prevent further contraction. We may thus define a quantity F which has been termed by Harkins the spreading coefficient:

$$F_s = \gamma_1 - \gamma_2 - \gamma_{12} \tag{8}$$

Evidently for those substances which do not spread on water, F_s has a negative value. When F_s is positive, the substance spreads on the water.

A typical hydrocarbon is tetradecane, $C_{10}H_{30}$, whose molecules consist of long chains. This substance does not spread on water and measurements show in fact that $F_s = -6.2$ dynes per cm.

There are large numbers of oils and fats, especially those of animal and vegetable origin, which, when placed on water, spread out to form extremely thin films of the order of 10^{-7} cm in thickness. It is found that the general characteristic of all such substances that spread is that they contain in their molecules certain groups of atoms which have an affinity for water and are therefore called hydrophilic. The most common of these groups is the —OH group or the —COOH group. If such a group is substituted for one of the hydrogen atoms in each of the molecules of a lower hydrocarbon, the effect is to increase the solubility of the substance in water.

The substances that spread as thin films upon water are thus substances whose molecules possess a composite surface, most of the molecule having very little affinity for water, thus being hydrophobic, while another portion of the molecular surface is hydrophilic. By spreading on the surface of the water, the molecules can thus arrange themselves so that the hydrophilic portion of each molecule comes into contact with water without bringing the hydrophobic portion in contact with the water. In most of the common fatty acids, the COOH group is at the end of the long chain. Thus when the molecules spread over the surface of the water, they become arranged on the water approximately vertically with the heads (hydrophilic groups) in the water and their tails (hydrophobic groups) packed side by side above the layer that contains the heads.

Because of the affinity of the hydrocarbon parts of the molecules for each other, the molecules spread out on the surface of the water only far enough for their heads to come in contact with the water. The surface tension of the water, therefore, is not decreased unless enough fatty acid is added to cover completely the surface with a monomolecular film. By measuring the volume of oil required to form a monomolecular film covering a given area, the thickness of the film can be calculated. This thickness is evidently the length of the molecules since these are arranged approximately vertically in the film.

By placing a known number of molecules on the surface and measuring the area to which the film spreads before the surface becomes that of pure water, the area per molecule can be measured. This gives the cross-section of the molecule. These experiments enable us to find the shapes of the molecules.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The spreading force F which characterizes any given absorbed film is entirely analogous to the pressure p which a gas or liquid exerts on the walls of a container. The pressure of a gas or liquid depends on the concentration and on the temperature. The relation between these quantities is usually referred to as the equation of state. Thus an ideal gas is characterized by the equation

$$pv = kT \tag{9}$$

where v is the volume per molecule. It is usually more convenient to express this equation in the term of n, the number of molecules per unit volume. The equation then takes the form

$$p = nkT \tag{10}$$

The analogy between p and F becomes very striking if we determine F which is defined by Equation (2) not from measurements of surface tension but directly by a surface balance. In this apparatus the surface of water in a long rectangular tray is divided by a floating barrier which is attached to the pointer of a balance so arranged that a horizontal force exerted on the barrier can be measured. When there is clean water on both sides of the barrier, the balance reads zero. A definite amount of an oil is placed on the water on one side of the barrier and this is confined to a given area by a second barrier parallel to the first. By moving the second barrier the film can be compressed so that it exerts a force on the balance and at the same time the area covered by the film can be measured. By progressively changing the area, by moving the second barrier, the force F may be measured as a function of a, the area per molecule. Any equation which expresses F as a function of a and T is thus an equation of state for the two-dimensional adsorbed film. If the adsorbed molecules do not exert any forces on one another, they should behave as an ideal two-dimensional gas. Thermodynamical reasoning then indicates that the equation of state should be

$$Fa = kT \text{ or } F = \sigma kT \tag{11}$$

where σ is the number of molecules per unit area in the adsorbed film. Comparison of these equations with Equations (9) and (10) shows the complete analogy between these two-dimensional gases and a typical three-dimensional gas.

The films produced on water by fatty acids and other oily substances have properties which indicate that they are two-dimensional liquids and solids rather than gases, for they do not spread indefinitely, but the value of F becomes zero when the surface concentration σ falls to a definite value. The mechanical properties of these films show clearly that they can exist in either the liquid or the solid state. For example, films of fatty acids on water, which is slightly alkaline and contains calcium ions, are definitely solid as is seen by the fact that when they are under even a very slight external pressure they can withstand considerable shearing stresses. On the other hand, a monomolecular film of cetyl alcohol, $C_{16}H_{33}OH$, on water behaves like a two-dimensional liquid; for even under high surface compression it can be made to circulate freely by blowing on it gently.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Measurements of Oil Films on Water

The measurements of oil films on water by the use of trays and movable barriers are limited to films which are insoluble in water and nonvolatile at ordinary temperatures. Such oils usually form films which act as either two-dimensional liquids or solids, and only in a few rather rare cases have films been found which behave like two-dimensional ideal gases.

There are many substances, however, which form an interesting type of film known as an expanded film. A good example is furnished by the fatty acids on water rendered slightly acid with hydrochloric acid (N/100 HCl). These films expand very easily as the surface pressure F is lowered; however, they do not expand indefinitely as a gas would, but the area per molecule, a, rises only to a definite limiting value when F falls to zero. I have been able to show that these films may be regarded as duplex films which consist essentially of a thin film of hydrocarbon liquid, with an upper surface having a surface tension γ_2 and a lower surface having a surface tension γ_{12}. If it were not for the hydrophilic groups of the molecules in the fatty acids, the spreading coefficient would be negative and the film would draw up into a lens. The hydrophilic groups are, however, located at the lower surface of the duplex film and in this surface they behave as a two-dimensional gas. The spreading force F_{12} due to these groups at the interface can only be effective in spreading the film out over the surface, provided that F_{12} is greater than the negative spreading force. Thus the equation of state for the duplex film as a whole is

$$(F-F_0)(a-a_0) = kT \tag{12}$$

where F_0 is the spreading coefficient in the absence of hydrophilic groups and a_0 is an empirical constant. The spreading force F_{12} at the interface is then given by

$$F_{12} = F-F_0 \tag{13}$$

Thus the equation of state at the interface itself is

$$F_{12}(a-a_0) = kT \tag{14}$$

In expanded films we thus have a case of a true gaseous film, but it is not the whole duplex film which is gaseous but merely its lower surface. The presence of the term a_0 in Equation (14), which was not present in the ideal two-dimensional gas, Equation (11), is entirely analogous to the b-term in the Van der Waals' equation of state of ordinary gases. This term arises from the fact that between the molecules there exist repulsive forces which act only when the molecules come into contact but which are effective in preventing two molecules from being in the same place at the same time.

By a different technique it is possible to study the nature of adsorbed films of organic substances which are soluble in water or are volatile. Gibbs' Equation (1) enables us to calculate σ, the number of adsorbed atoms, if we have

Digitized by Google Original from UNIVERSITY OF MICHIGAN

experimentally determined values of F as a function of the concentration of the dissolved substance in the water. The values of F are determined according to Equation (2) by the changes in surface tension. The value of p in Equation (1) should be considered the osmotic pressure of the dissolved substance in the water, or, if the solutions are not ideal, p should be regarded as the fugacity defined by G. N. Lewis. We can then express F as a function of σ and T and so obtain the equation of state of the adsorbed film on the surface, even if this film is soluble or volatile. It has been possible to show from published data on the surface tensions of aqueous solutions of organic substances that when these solutions are sufficiently dilute the adsorbed film behaves as a two-dimensional gas, while with higher concentrations the film condenses, in other words, becomes liquid or solid.

The interfaces between oil and water are far more important, from a technical point of view, than are the free surfaces of water. For example, in emulsions we have to deal with adsorbed films at the interface between oil and water. The biologist is also concerned with such interfaces as the walls of living cells in an aqueous medium.

For these reasons, and also because interfacial phenomena should be relatively free from the type of complications which we have come across in considering expanded films, Dr. Blodgett and I during the last year or so have been making extensive experimental and theoretical studies of the adsorbed molecules at the interface between oil and water. This work is still in progress and results have not yet been published except in a preliminary form.[2] I will give you only a brief account of our results so far. Perhaps you will find the experimental technique, however, of greater interest than the results thus far obtained.

In these studies we have used a pure hydrocarbon mineral oil, a so-called white oil (Squibb's Petrolatum), in which we have dissolved small amounts of stearic acid in concentrations, expressed in parts by weight w, ranging from 10^{-6} to 10^{-2}.

Small amounts of these solutions placed upon water show phenomena of great interest. The results depend remarkably on whether the water is acid or alkaline, and when alkaline, minute traces of calcium or magnesium salts modify the results profoundly. Let me describe the phenomena as they occur on water containing sodium hydroxide (1/50 normal).

When very dilute solutions of stearic acid in mineral oil (w ranging from 10^{-5} to 5×10^{-5}) are placed on alkaline water, the drops are at first in the shape of lenses, which may be as much as 3 mm thick. It will then be noticed that the lenses gradually increase in diameter becoming thinner as they slowly spread. The diameter, however, does not continue to increase indefinitely, but reaches a limiting value. The experiments show that this limit is reached when all of

---

[2] "Mechanical Properties of Monomolecular Films," by Dr. Irving Langmuir, *J. Franklin Inst.* vol. 218, August 1934, pp. 143–171.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the stearic acid in the oil has diffused to the interface between the oil and the water, and that the final area covered by the lens is proportional to w, the amount of stearic acid which is present. From the number of molecules present and the area covered we can calculate a, the area occupied by each molecule at the interface. These experiments show that $a = 88 \times 10^{-16}$ cm² per molecule of stearic acid. We must compare this with the area 20.4×10^{-16} which is the area occupied by the stearic molecules when they are closely packed on the water surface. This fact alone indicates that the adsorbed film at the interface is a gaseous film.

It has been possible to calculate the diffusion coefficient of the stearic acid through the oil from measurement of the rate at which these oil lenses increase in diameter. When the diameter does not exceed about three-quarters of the final diameter, the theory gives the equation

$$d \log_e \Delta/dt = n^2 a^2 D/\pi \qquad (15)$$

where D is the diffusion coefficient; n is the initial concentration before spreading begins, measured as molecules per cubic centimeter; A is the area of the lens at any time t; and a is the area per molecule occupied at the interface. This equation agrees excellently with experiment. It shows that the rate of spreading increases in proportion to the square of the original concentration.

With solutions stronger than $w = 10^{-4}$, the lenses spread too rapidly to permit measurement. When concentrations from 0.001 to 0.006 are used, the films become so thin that iridescent colors appear on the surface, the color being uniform over the whole surface of the film. Since every molecule of the stearic acid goes to the interface and occupes the area a, the thickness b of the film can be calculated by the equation,

$$nab = 1 \qquad (16)$$

n being as before the original concentration of the stearic acid in the lens.

Use of Colored Oil Films

These colored oil films are very convenient to work with for the color enables us to determine the thickness b, so that, if we have solutions of known concentration, n, we can calculate a by means of Equation (16). The method of finding the thickness of the film from the color consists in matching the color of the film against that of a comparison film. A comparison oil was first made by oxidizing a white mineral oil, or even a lubricating, oil, by heating it in an open dish on a hot plate until it smokes. During this process drops of oil are removed from time to time and placed upon a clean water surface. At first the drops form lenses. As oxidation proceeds the lenses spread out into colored films. The oxidation is continued until the films become so thin that the color nearly disappears. A drop of known volume (from a calibrated pipette) is then placed

Digitized by Google Original from UNIVERSITY OF MICHIGAN

on water in a large tray. By moving a barrier supported by the edges of the tray the area of this oil film can be decreased and as this is done the color changes from the original faint yellow to a series of other colors. In this way the color can be brought to match that of any other colored film whose thickness it is desired to measure.

The thickness of the film of the comparison oil can always be determined by dividing the volume of the drop by the area occupied by it on the tray as determined by the position of the barrier. When the color of the comparison film is the same as that of the film to be studied, then the thickness is the same if the order of the color is the same and if the refractive index of the oil is the same. It is easy to tell whether the order is the same by seeing whether the comparison oil and the oil being tested are the same in color when viewed at several different angles of incidence.

The values of a determined from these values of b by means of Equation (16) are found to be the same (88×10^{-16} cm^2) as for the lenses of the very dilute solutions for which $w = 10^{-5}$. These results prove that there is no measurable solubility of the film on alkaline water in the mineral oil so that all the dissolved substance becomes adsorbed at the interface. Very minute amounts of calcium in the water, even as little as 10^{-5} molar, are sufficient to change completely these results. The film at the interface, instead of being gaseous, then becomes solid and very rigid and the area per molecule is about 20×10^{-16} Such sensitivity to the effect of calcium ions suggests a close analogy between these films and the walls of living cells. The biologist finds that the conditions of living cells are enormously affected by the ratio of the concentration of calcium and sodium ions. The study of the simple relationships at these oil-water interfaces should help to throw light upon these fundamental biological phenomena.

I have said that acid solutions behaved quite differently. When drops of solutions of stearic acid in mineral oil are placed upon dilute HCl (1/100 N), the adsorbed film of stearic acid at the interface between the oil and the water shows a definite solubility in the mineral oil. This solubility not only increases with rising temperature, but depends greatly upon the spreading force F_{12} at the interface.

This relation is given by

$$\log_{10} [F_{12}^2/w] = -0.465 + (1740 - 15.8F_{12})/T \qquad (17)$$

We have developed two methods for measuring F_{12}. One is suitable for measuring values of F_{12} less than 12 dynes per centimeter, and the other method can be used for larger values.

With sufficiently dilute solutions of stearic acid in Petrolatum I have said that a lens is formed on the surface of the water. At the outer edge of this lens three surfaces meet, namely, the interface between the air and the water (of surface tension γ_1), the interface between the air and the oil (of surface tension

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

γ_2), and finally the interface between the oil and the water (surface tension γ_{12}). If α is the angle which the first two of these surfaces make with one another, then the fundamental laws of surface tension require that

$$\cos \alpha = (\gamma_{12}^2 - \gamma_1^2 - \gamma_2^2)/2\gamma_1\gamma_2 \qquad (18)$$

If the lens does not contain too much stearic acid, no acid escapes from the lens onto the surrounding water surface so that the surface tension γ_1 remains constant and has a definite characteristic value at any temperature. Experiments show that the surface tension γ_2 of the mineral oil is not perceptibly modified by the presence of stearic acid in the oil, so that γ_2 is also constant at any temperature. Thus if we measure experimentally the contact angle α, we may calculate the value of γ_{12} by Equation (18). We first carry on experiments of this kind with pure Petrolatum and then with a solution of stearic acid in Petrolatum; the difference between the first and second of these values of γ_{12} by an equation analogous to Equation (2) can be used to calculate F_{12}, the spreading force of the adsorbed stearic-acid molecules in the interface between the oil and the water.

This method of determining F_{12} can only be used when the spreading coefficient F_s, as given by Equation (8), has negative values; that is, when $\gamma_2+\gamma_{12}$ is greater than γ_1. If F_0 is the value of the spreading coefficient of the pure mineral oil on water, then for a solution of stearic acid in mineral oil the spreading coefficient will be

$$F_s = F_0 - F_1 + F_{12} \qquad (19)$$

Since F_s must be negative, F_{12} must be less than $F_1 - F_0$. If F_0 is equal to -12, we can measure values of F_{12} by this method only up to values of $+12$ unless we place upon the water surrounding the lens a stearic-acid film under pressure so that we have positive values of F_1.

Duplex Film Method of Measurement

The second method of measuring F_{12}, which we may call the duplex film method, can be used when the contact angle α is equal to zero. This condition is fulfilled when sufficiently strong solutions of stearic acid in oil are used. The oil then spreads as a duplex film, and in this case since F_s is zero, we have

$$F_{12} = F_1 - F_0 \qquad (20)$$

Thus if the oil is allowed to spread on clean water, the duplex film method can be used only when $F_{12} = -F_0$. However, by allowing the oil to spread on a surface on which there is already a stearic-acid film under compression, higher values of F_{12} may be obtained.

Let us suppose that we place a series of fairly concentrated solutions of stearic acid in Petrolatum on water. When the oil comes into contact with water, the stearic acid diffuses to the interface. As soon as F_{12} rises above 12, F_s becomes positive and the lens spreads out into a duplex film, but this brings more and more of the dissolved molecules to the interface so that gradually the con-

Digitized by Google Original from UNIVERSITY OF MICHIGAN

centration of the acid in the oil decreases to the point where F_{12} falls to 12; spreading then ceases. If we let n_0 be the final concentration within the oil of the oil film when spreading has ceased, and we let n be the initial concentration before the oil was placed upon the water, then since the original excess concentration has been used up by supplying molecules to the interface, we have the relation

$$(n-n_0)a = 1/b \tag{21}$$

We may use this equation to determine n_0 and a from values of the thickness b, obtained by the colored film method, for a series of solutions of different concentrations n. If we plot the values of $1/b$ against n, we obtain points that lie along a straight line whose intercept on the n-axis gives n_0 and whose slope gives the value of a.

These two methods give results which agree with one another perfectly in the range in which they can both be used. The data on which Equation (17) was based were made by measurements by these two methods.

Experiments by two different methods have shown that stearic acid in solution in Petrolatum exists in the form of double molecules which satisfactorily obey the ideal gas laws of solution. We can thus apply Gibbs' equation to calculate the equation of state of the adsorbed film of stearic films at the interface and in this way find

$$F(a-a_0) = kT \tag{22}$$

where a_0 has the value 25×10^{-16} sq. cm. This result is in complete agreement with the theory of expanded films.

With sufficiently high values of F_{12} and sufficiently low temperatures, data were obtained which indicated that the adsorbed film at the interface is no longer gaseous but condenses into a liquid film for which the area per molecule (assuming normal molecular weight) is 25×10^{-16}. The transition between the gaseous and liquid films makes a definite break in the curves which is entirely analogous to the sudden change in volume which a liquid undergoes in being changed to a vapor at its boiling point.

I think the main interest in these results is that they make it clear that at the interface between oil and water we have a real two-dimensional world which is almost completely analogous to the three-dimensional world with which we are more familiar. The methods that I have outlined should be capable of supplying accurate data by which all the thermodynamical relations that govern these films may be obtained. Dr. Blodgett and I intend to study several different substances and particularly wish to determine quantitatively how the values of F_{12} are modified by the presence of hydrogen and hydroxyl ions. When we have made such measurements, it should be possible to calculate by Gibbs' equation the number of hydrogen or hydroxyl ions that go into the structure of the film at the interface. Of course our choice of stearic acid was merely arbitrary; it simply represents a type of an adsorbed substance.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Studying Monomolecular Films on Solid Surfaces

Much knowledge of monomolecular films can be obtained by transferring them to solid surfaces and then studying their mechanical properties. For example, if we have a surface of glass on which we have placed a monomolecular film of fatty acid, we find that the film acts as a lubricant so that we may measure the coefficient of friction as a sensitive test of the presence of such films. Furthermore we may place on this film on glass a drop of some liquid which does not wet the surface and can measure the contact angle that the surface of the liquid makes with that of the solid where the surfaces come in contact. From a measurement of this angle it is possible to calculate the work of adhesion W_s which is given by the equation,

$$W_s = \gamma_2(1+\cos B) \tag{23}$$

where B is the contact angle which is zero if the liquid wets the solid surface.

There are many ways of putting monomolecular films on a solid surface. A glass slide may be dipped in benzol in which a small amount of stearic acid has been dissolved. The film which is thus formed on the glass cannot be washed off even by hot benzol and it is far less volatile in vacuum than stearic acid itself. This shows that the stearic-acid molecules are held very firmly to the glass. A hardened steel sphere of small diameter, pressed against this surface with a force which gives a local pressure of over 30,000 kg per sq. cm, can be moved back and forth along a line on this surface several hundred times before it wears through such a monomolecular film. The coefficient of friction is a very small fraction of that which is observed in the absence of the film.

We have found that monomolecular films of fatty acids can be transferred from a water surface to a glass surface. Dr. K. B. Blodgett has developed this technique to a point where any number of layers of stearic acid can be transferred to glass or metal. To get the best results the film of stearic acid should be placed on slightly alkaline water containing a low concentration of calcium ions. The film is then very rigid and, by compressing it, it can be forced up onto a glass slide while this is being removed from the water. The slide then comes out of the water dry and if it is pushed down again into the water a second layer of these calcium-stearate molecules can be placed on the glass, but the molecules are turned upside down. On withdrawing the glass a third layer is formed with molecules oriented as in the first layer.

These multimolecular films appear to have extraordinary and remarkably uniform properties. It is the only type of surface that I know of that is not wettable by water or by ordinary organic liquids. We hope that a measurement of the contact angles of various liquids on these surfaces will give us much more detailed information regarding their nature. We have also found that by applying a sufficient number of these layers, interference colors can be observed and accurate measurements can be made of their thickness by optical means. It should be of much interest to physicists to measure the elliptic polarization

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

of light reflected from such surfaces. Diffraction of X-rays by these films should also be of interest.

Mr. Schaefer and I are also engaged in making studies of the rôle played by monomolecular films in lubrication. We have devised several new types of apparatus by which we can measure the stability and wearing qualities of monomolecular films and the rapidity with which such films are produced on bearing surfaces. All the results indicate that the remarkable effects that have been obtained with so-called highpressure lubricants are dependent upon the formation of unusually stable monomolecular films on the surfaces.

Studies of Adsorbed Caesium Atoms

I have told you that the interesting phenomena observed with films of thorium on tungsten filaments can be understood better after a consideration of the properties of films of caesium on tungsten. Caesium is the most electropositive element that is known; that is, it has less affinity for electrons than any other metal. This is also indicated by its ionizing potential, 3.9 volts, which is lower than that of any chemical element.

The heat of evaporation of electrons from tungsten corresponds to 4.6 volts; that is, it is as great as the work that has to be done to make an electron move against a potential of 4.6 volts. It is therefore not surprising that experiments show that every caesium atom which strikes a tungsten surface at high temperature loses its electron to the tungsten and escapes as a positively charged caesium ion. This may be looked upon as being caused by the fact that the electron affinity of the tungsten is 0.7 volts greater than that of the caesium ion. The electric current that thus flows from the tungsten is a quantitative measure of the number of atoms of caesium that strike the filament. Since currents of 10^{-17} amp. can be measured by an electrometer, it thus becomes possible to detect a pressure of caesium vapor so low that only 100 caesium atoms per second strike the surface of a filament.

The escape of the caesium ions from the tungsten surface is an evaporation phenomenon and thus below about 1000 deg. K the atoms that strike the surface accumulate. As the surface concentration σ builds up, the rate of atom evaporation increases, but if the filament is at room temperature, there is no appreciable evaporation until the surface becomes covered by a complete monatomic film of caesium.

Dr. J. B. Taylor and I have worked out two methods for measuring quantitatively the number of atoms of caesium that are adsorbed on the filament at any time. When the number of adsorbed atoms is less than 0.08 of the number necessary to form a complete film, a sudden heating of the filament to high temperature causes all the adsorbed caesium atoms to evaporate as ions. If the filament is surrounded by a negatively charged cylinder, this sudden burst of ions produces a momentary current which can be measured by a bal-

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

listic galvanometer or electrometer. With a good electrometer the current produced by 100 ions will give a measurable reading. This method of detecting caesium atoms on a filament is so extraordinarily sensitive that, if desired, it should be possible, by allowing the caesium atoms to accumulate on the filament for 24 hr, to detect the presence of caesium vapor even with pressures as low as 10^{-26} atmospheres, which is the pressure that would be produced in a large space if there is a concentration of caesium vapor corresponding to one atom of caesium in every five cubic meters of space.

The second method of measuring σ involves the evaporation of adsorbed atoms as atoms, in the presence of a retarding field which prevents the escape of ions. This burst of atoms falls on a parallel neighboring tungsten filament heated above 1300 deg. from which these atoms escape as ions. The ballistic kick of current from this second filament thus measures σ on the first filament.

Some idea of the magnitude of the forces that hold the caesium atoms on the surface of the tungsten is to be had by considering that the rate at which caesium evaporates from the tungsten surface at 1000 deg. K is no greater than that at which it leaves a surface of metallic caesium at room temperature. This means that the forces that hold the caesium atoms on the tungsten are about three times greater than those which hold the atoms of metallic caesium together.

Such large forces between the adsorbed caesium atoms and the underlying tungsten surface are to be expected as a result of the fact that the caesium tends to lose its electron when close to the tungsten surface. Thus the positively charged caesium ion induces into the conducting tungsten surface a negative charge, which exerts a force of attraction on the ion (the image force) equal to $e^2/4x^2$, where x is the distance of the ion from the surface. This image force is of ample magnitude to account for the strong forces holding caesium on tungsten.

I have pointed out that the remarkable ability of a tungsten filament to convert caesium atoms into ions depends upon the fact that the ionizing potential of caesium is less than the heat of evaporation of electrons from tungsten. Further support for this theory is obtained by considering other metals than caesium and other filaments than tungsten. It has been found that potassium and rubidium which have ionizing potentials less than 4.6 volts also form positive ions when their atoms strike a hot tungsten surface, but sodium, which has an ionizing potential of 5.1 volts, gives no appreciable positive current, neither does lithium. By using a thoriated-tungsten filament the heat of evaporation of electrons from the filament can be lowered from 4.6 volts to 3.1; it is then lower than the ionizing potential of caesium. In agreement with this fact we find that even caesium atoms do not readily form ions on a tungsten surface completely covered with thorium atoms. On the other hand, by forming on the tungsten surface a film of adsorbed oxygen atoms,

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the electron emission from the tungsten is greatly reduced and the heat of evaporation goes up to 5.6 volts. A filament with such a film is capable of yielding positive ions even with atoms of sodium and lithium.

I have often spoken of a complete monatomic film. If we are dealing with adsorption on a strictly plane surface, it is evident, since atoms and molecules are not easily compressible, that there is a rather definite limit to the number of atoms that can be crowded into a single layer upon a surface. If we let σ_1 represent this maximum number, and let σ be the number actually present on a surface at any time, the ratio σ/σ_1, which we may call θ, represents the fraction of the surface covered. The experiments with caesium atoms on tungsten indicate that on pure tungsten filaments the number of atoms that can be adsorbed tends to reach a very definite upper limit as the temperature of the filament is lowered and the pressure of the caesium vapor is raised. We find that the maximum number, σ_1, is 3.56×10^{14} atoms per sq. cm which is just one-quarter the number of tungsten atoms per unit area on the surface of a tungsten crystal. This agrees well with the fact that the diameter of the caesium atom is closely double that of the tungsten atom.

If the temperature of the filament is less than about 10 deg. above the temperature of the bulb which contains saturated caesium vapor, it is possible to get values of σ which rapidly increase above σ_1. The experiments show, however, that these atoms which condense in the second layer evaporate about six times faster than they would from a surface of pure caesium. Clearly then there is no justification for assuming a gradual transition in properties between the tungsten and the caesium as successive layers of atoms are applied. The change brought about by the formation of the first layer is greater than the whole difference between a tungsten surface and a caesium surface.

The forces which hold adsorbed atoms on surfaces in characteristic cases of adsorption are usually far greater than those which act between the adsorbed atoms themselves. If this were not so, we would normally be dealing with the case where crystal nuclei rather than adsorbed films are formed. The effect of these strong forces which originate from the underlying surface is to polarize the adsorbed atoms, and thus if the atoms are all of the same kind, they tend to become similarly oriented dipoles which repel one another with forces which vary inversely as the fourth power of the distance between them. These dipole forces have a range of action far greater than the forces directly responsible for adsorption. Such repulsive forces should cause the equation of state for the adsorbed film to depart considerably from that of an ideal gas.

With the powerful electrical forces characteristic of adsorbed caesium atoms on tungsten, these repulsive forces are particularly strong. Fortunately it is possible experimentally with these caesium films to obtain all the data necessary for a complete measurement of these forces.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

The force f between two adsorbed atoms which act as dipoles of moment M is given by

$$f = (3/2)\, M^2/r^4 \tag{24}$$

where r is the distance between atoms.

We have already seen that the ideal gas law given by Equation (11) corresponds to the case where there are no forces between the adsorbed gases. The effect of the dipole forces is then to cause deviations from the ideal gas laws which may be calculated by the Clausius Virial equation,

$$F = \sigma kT + (1/4)\sigma\, \Sigma\, (rf) \tag{25}$$

where the summation extends over all the adsorbed atoms which act on any one of them. We cannot directly measure the mechanical force F of an adsorbed film on a solid surface, but fortunately we do not need to do so in order to make use of this thermodynamic function since we may combine Equation (25) with Gibbs' Equation (1) and so eliminate F. Similarly it is possible in principle to eliminate f between Equations (24) and (25). The rate of evaporation ν_a of caesium atoms from a tungsten surface can thus be expressed as a function of σ, T, and M. It has, in fact, been possible to derive a definite equation giving the relationship between these quantities for caesium on tungsten.

This means that from measurements of the rate of evaporation ν_a of caesium atoms from a tungsten surface we can determine M as a function of σ and T.

The adsorbed caesium atoms on the surface constitute an electric double layer across which there is a difference of potential V, the so-called contact potential, which is related to the dipole moment by the equation.

$$V = 2\pi\sigma M \tag{26}$$

Furthermore, the rate of evaporation of electrons ν is related to the contact potential V by the Boltzmann equation,

$$\nu_e/\nu_w = e^{Ve/kT} \tag{27}$$

where ν_w is the rate of evaporation of electrons from pure tungsten.

From experimentally obtainable values of ν_e, by measuring the electron emission of the tungsten filament covered with the adsorbed film, we can thus determine V and since we know σ we can calculate M as a function of σ and T.

It has also been possible to work out a thermodynamic relationship between M, the dipole moment and ν_p, the rate of evaporation of positive caesium ions from the surface, as a function of σ and T.

Dr. Taylor and I have made measurements of ν_a, ν_e and ν_p, and from each of these sets of measurements we can calculate M as a function of σ and T. The experiments show that values of M obtained in these three entirely different ways are in agreement with one another at least when the filament is more than half covered with caesium atoms.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

This agreement should indicate that the dipole forces given by Equation (24) are the only forces which we need to consider in order to understand fully the variation of the electrical and thermodynamic properties of the caesium film as we increase the amount of caesium σn the surface up to $\theta = 0.5$. It has been possible to apply the same theory to thorium films on tungsten so that from the rate of evaporation of electrons it has been possible to calculate the rate of evaporation of the neutral atoms of thorium.

Dr. Taylor and I have recently carried out investigations of the adsorption of caesium on tungsten surfaces which were previously covered to various degrees with thorium atoms. The results are extremely interesting. They show that the first caesium atoms which are adsorbed fit into the spaces between the thorium atoms, but that as more caesium is added, the additional caesium atoms are adsorbed on top of the thorium atoms. The caesium and thorium atoms repel one another with different forces from those acting between the caesium atoms. Because of this variety of ways in which the caesium can be adsorbed, there is no longer a definite limiting value σ_1 such as there is on pure tungsten.

We have also begun experiments on which we place known numbers of oxygen atoms on a tungsten surface before adsorbing the caesium. Here the oxygen atoms act as negative dipoles which attract the positive dipoles of the caesium. There is therefore a tendency to form clusters of caesium atoms around each oxygen atom. These phenomena are far more complicated than are observed with caesium alone on tungsten, but even more valuable in leading us to a full knowledge of adsorption phenomena. Films of caesium held on to tungsten by oxygen atoms enable us to produce the most efficient source of electrons for use in vacuum tubes. Dr. Kingdon has been able to construct hundreds of high-vacuum radio receiving tubes in which the cathode emits 0.2 amp. per sq. cm or more at temperatures of only 900 deg. K. It has been possible to obtain long lives with such cathodes, but in these days when alternating currents are used for heating the cathodes of receiving tubes there does not seem to be sufficient need for such tubes as to warrant their commercial development.

The understanding of the electron emission from caesium atoms adsorbed on surfaces has, however, been of vital importance in the development of the highly efficient photoelectric tubes which are now widely used industrially.

In this summary of our studies of adsorption phenomena I have endeavored to show that we have to deal with a whole new world of two-dimensional phenomena. We cannot expect that in all cases the phenomena will be simple any more than we can expect all chemical phenomena in the three-dimensional world to be simple. I hope, however, that I have been able to convey to you some of my faith that knowledge in this field will lead to many important scientific and technical discoveries.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

TWO-DIMENSIONAL GASES, LIQUIDS AND SOLIDS[1]

Science
Vol. LXXXIV, No. 2183, 379, October (1936).

WE LIVE in a world of three dimensions. We measure objects by their length, breadth and thickness. The position of a point can be described by three coordinates, x, y, and z. We can not escape from the inside of a spherical surface except by passing through it, but if we are standing in a circle on a surface we escape from it by stepping over it.

It is amusing to try to imagine a fourth dimension. We can reason that if we could travel into it, we could escape from the inside of a sphere without going through its surface.

In the special theory of relativity, Einstein has given us reasons for looking upon time as a kind of imaginary fourth dimension which differs from any of the ordinary dimensions of space much as the number one differs from the imaginary number $\sqrt{-1}$.

In the general theory of relativity, there are suggestions that the effect of gravitation is to warp four-dimensional space-time in a fifth dimension, very much as we have to warp a map of Europe to make it fit onto a globe representing the earth.

Poincaré in an interesting book, *Science and Hypothesis*, attempted in 1903 to trace the probable development of science on the earth if it had happened that the earth's atmosphere, like that of Venus, had been perpetually cloudy. Without ability to observe the stars and sun, mankind would have persisted for long in a belief that the earth is flat. If a pioneer among scientists had made the statement that the surface of the earth has no edge or boundary but yet has a limited area, he would have been disbelieved; for these two statements seem contradictory to those who believe in a flat earth. The difficulty disappears, however, if it is recognized that the surface of the earth is bent into a spherical surface by being warped in a third dimension.

When some forms of the relativity theory tell us that space has no boundaries and yet has a limited volume, we are similarly perplexed. The warping of our space in a fourth or fifth dimension, however, can remove these difficulties, at least for some people (the newspapers say ten).

---

[1] Address delivered at the Mark Hopkins Centenary, Williams College, October 10, 1936.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Many of you perhaps have seen the little book entitled ***Flatland***, written in 1885 by an author who gives the name A. Square, but who is said to be Edwin A. Abbott. A race of people is pictured who live in two dimensions. One of the inhabitants argues that there can be no third dimension, just as we argue that there can be no fourth dimension.

Of course, no one can seriously maintain the existence of a real fourth dimension of space, which is like the three that we already are familiar with.

To-day, however, I propose to tell you of a real two-dimensional world in which phenomena occur that are analogous to those described in ***Flatland***. I plan to tell you of the behavior of molecules and atoms that are held at the surfaces of three-dimensional solids and liquids. The chemist has long described molecules that are held in this way on surfaces as adsorbed molecules. I will show you that we can have adsorbed films which really constitute two-dimensional gases, two-dimensional liquids and two-dimensional solids.

Hydrogen and carbon combine to form a very interesting class of substances called hydrocarbons. Most of these are stable and relatively inert. A good example of a compound of this kind is a substance called hexadecane, which has a formula $C_{16}H_{34}$, the carbon atoms being arranged in a long chain. Purified mineral oil, such as petrolatum, is a hydrocarbon having similar properties. It is not appreciably volatile and is insoluble in water.

When a drop of such a liquid is placed upon water, it floats on the surface as a lens which has a definite circular boundary where oil, water and air meet. Although the force of gravity tends to make the oil spread out over the water in a thin film, the lenses formed by petrolatum are about 4 mm thick. There must therefore be a force of considerable magnitude which prevents the oil spreading. Measurements show that this force amounts to about 12 dynes per cm.

There are large numbers of oils and fats, however, which when placed on water spread out to form extremely thin films of the order of 10^{-7} cm thick. It is found that the general characteristic of all such substances that spread is that they contain in their molecules certain groups of atoms which have an affinity for water and are therefore called *hydrophilic*. The most common of these groups is the —OH group or the —COOH group. If such a group is substituted for one of the hydrogen atoms in each of the molecules of a lower hydrocarbon, the effect is to increase the solubility of the substance in water.

The substances that spread as thin films upon water are thus substances whose molecules possess a composite surface, most of the molecule having very little affinity for water, thus being *hydrophobic*, while another portion of the molecular surface is hydrophilic. By spreading on the surface of the water, the molecules can thus arrange themselves so that the hydrophilic portion of each molecule comes into contact with water without bringing the hydrophobic portion in contact with the water. In the common fatty acids,

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the COOH group is at the end of the long chain. Thus when the molecules spread over the surface of the water, they become oriented on the water so that they are approximately vertical with their heads (hydrophilic groups) in the water and their tails (hydrophobic groups) packed side by side above the layer that contains the heads.

Because of the affinity of the hydrocarbon parts of the molecules for each other, the molecules spread on the surface of the water only far enough for their heads to come in contact with the water. The surface tension of the water, therefore, is not decreased unless enough fatty acid is added to cover completely the surface with a monomolecular film. By measuring the volume of oil required to form a film covering a given area, the thickness of the film can be calculated. This thickness is evidently the length of the molecules, since these are arranged nearly vertically in the film.

By placing a known number of molecules on the surface and measuring the area to which the film spreads before the surface tension is lowered below that of pure water, the area per molecule can be measured. This gives the cross-section of the molecule. These experiments enable us to find the shapes of the molecules, and prove that the molecules of the higher fatty acids such as stearic acid $C_{17}H_{35}COOH$ in a film on water have a cross-section of about 20×10^{-16} sq. cm or an average diameter of about 4.5×10^{-8} cm; while the length of the molecule is about 24×10^{-8}, or more than five times the diameter. This is quite in accord with the known chain-like arrangement of the carbon atoms.

Experiments of this kind are best carried out by using a large shallow tray which is filled to its brim with water. Movable strips of metal placed across this tray serve as barriers to confine the film that is produced by adding oil to the surface. To measure the force F per unit length which the film exerts on the barrier, one of the barriers is replaced by a floating strip of paper made waterproof by paraffin, which is attached to the vertical pointer of a balance placed above the tray. The leakage of the film around the ends of the floating barrier is prevented by connecting the barrier with neighboring points on the rim of the tray by paraffined silk threads which float on the surface of the water. The balance is adjusted so that it reads zero when there is clean water on both sides of the barrier. A definite minute amount of a substance such as a fatty acid is placed on the water on one side of the floating barrier by applying measured drops of a dilute solution of the substance in a volatile solvent, such as benzene. The film is confined to any desired area by a second barrier which extends across the tray. Dividing the area between the fixed and floating barriers by the number of molecules which have been placed on the surface, we obtain the area per molecule which we denote by a. The weights which must be placed on the pan of the balance in order to hold the floating barrier in a fixed position give us the force F (per unit length) exerted by the film. By progressively changing the area by moving

Digitized by Google Original from UNIVERSITY OF MICHIGAN

the second barrier, the force F may be measured as a function of a, the area per molecule.

An elementary experiment in physics consists of establishing the validity of Boyle's law (which states that the pressure of a gas is inversely proportional to its volume) by placing a gas in a cylinder in which there is a movable piston by which any desired force can be applied. An equation which expresses the pressure in terms of the volume and temperature is called an equation of state. For ideal gases it is found in this way that

$$pv = kT \tag{1}$$

where p is the pressure, v is the volume of the gas divided by the number of molecules, T is the absolute temperature, and k is a universal constant 1.37×10^{-16} when expressed in the usual units. It is sometimes more convenient to express this equation in terms of n, the number of molecules per unit volume of gas. The equation then takes the form

$$p = nkT. \tag{2}$$

I hope you see the close analogy between the experiments in which a gas is confined in a cylinder having a movable piston and the experiment in which we place a monomolecular oil film on the surface of water in a tray, which is provided with a floating barrier which can exert any desired force on the film. The floating barrier thus corresponds to the piston in the three-dimensional experiment. We may thus look upon an equation which gives F in terms o. a as the equation of state for the two-dimensional film on the surface of the water.

The justification for regarding the film as having only two dimensions is that it consists of a single layer of molecules, so that the motions of the barrier do not cause the molecules to climb up on one another and so move into the third dimension.

With this concept of the molecules existing in a two-dimensional film, it is possible by well-established principles of thermodynamics to show that if the absorbed molecules do not exert any force on one another, they should behave as an ideal, two-dimensional gas; and that the equation of state of this two-dimensional gas should be given by

$$Fa = kT \tag{3}$$

where k has exactly the same value as is found for a three-dimensional gas. You see the form of this equation is the same as that of Eq. (1), the force F corresponding to the pressure p, the area per molecule a corresponding to v.

It is often convenient to describe a monomolecular film in terms of σ which may be defined as the number of molecules per unit area, which is evidently the reciprocal of a. Thus the equation of state can also be written

$$F = \sigma kT. \tag{4}$$

This equation is evidently entirely analogous to Eq. (2).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Films produced on water by non-volatile and insoluble fatty acids have properties which indicate that they are two-dimensional liquids and solids rather than gases, for they do not spread indefinitely; the value of F becomes practically zero when the surface concentration σ falls to some definite value. This is just what would happen in the three-dimensional experiment with the cylinder and piston when the cylinder is completely filled with a liquid. If we apply considerable pressure to the piston, the volume decreases only a very little; and if we lower the pressure, the volume does not increase indefinitely. The molecules of the two-dimensional film are held together by cohesive forces which originate from the interaction by the hydrocarbon chains, which by themselves tend to draw the film into a lens just as they do in a case of a pure hydrocarbon.

Solids and liquids in a three-dimensional world do not differ very greatly in volume or density nor in compressibility. The main difference is that a solid has the property of rigidity; that is, it can withstand shearing stresses. Oil films on water which are not two-dimensional gases can be described as condensed films, for the molecules are tightly packed against one another either because of external pressure or because of the cohesion between the molecules. These condensed films can exist in a solid or liquid state. This can be shown by their enormous differences in withstanding shearing stresses. For example, if particles of talc are dusted upon a liquid film, these particles circulate freely over the surface if one blows lightly upon the surface. In the case of solid films, however, the talc particles are held rigidly in definite positions on the surface by the rigidity of the film. Many intermediate states can be observed, for example, where the talc particles will move only slowly even when a considerable force is applied by a strong blast of air. Such films evidently constitute a two-dimensional liquid of high viscosity.

We have recently constructed a simple apparatus to determine these mechanical properties of condensed films. A light aluminum disk is suspended at its center by a fine tungsten wire from a support which permits the rotation of the tungsten wire around its axis. This disk is lowered until it comes in contact with the surface of the water in the tray. An oil film is then placed on the water and subjected to any desired pressure by means of a barrier. The upper end of the tungsten wire is then rotated through a definite angle. If the film is liquid, the disk will also rotate through the same angle, and the length of time that it takes to do so is a measure of the viscosity. If the film has the properties of a two-dimensional solid, the rotation of the support will cause only a small elastic rotation of the disk, which corresponds to an angular displacement very much less than that of the support.

Experiments of this kind show that films of stearic acid on pure water, even if it is made alkaline by potassium hydroxide, are always liquid. Many previous investigators have found that such films on alkaline water are solid. It now appears that the observed rigidity was caused by extremely minute

Digitized by Google Original from UNIVERSITY OF MICHIGAN

traces of impurities of divalent or trivalent elements in the water. One part in one hundred million of such impurities may be sufficient to make stearic acid films solid.

The films that I have been speaking of are those that form at the free surface of water; that is, at an interface between water and air. Such films have been quite extensively studied in recent years by a number of investigators.

If a thick layer of a pure hydrocarbon is placed upon water, the interface that forms the boundary between the hydrocarbon and the water is also a surface in which molecules can become adsorbed. The properties of these interfacial films are simpler than those of films on the free surface of water and exhibit in a more striking way the three possible states of a two-dimensional film (solid, liquid or gas). These films are also perhaps of greater fundamental interest, for their study throws light on many problems of biology, particularly those that characterize the walls of living cells.

The investigation of these interfacial films has been greatly facilitated by several new experimental techniques which have recently been developed by Dr. Katharine B. Blodgett. I can illustrate these by telling you what happens when a small amount of stearic acid is dissolved in a non-volatile hydrocarbon, such as petrolatum, and a drop of this is placed on alkaline water.

If only one part of fatty acid in several million parts of petrolatum is used, the drop remains as a globule on the surface; but the contact angle that the water makes with the oil gradually changes as the stearic acid slowly diffuses to the interface.

If one part in a hundred thousand is used, it is observed that the drop increases in size at first slowly, then with increasing rapidity; until quite suddenly it reaches a limiting size and stops spreading. The area to which the drop spreads is proportional to the amount of stearic acid that is placed in the drop but is independent of the amount of petrolatum that is in the drop. This proves that on alkaline water every molecule of stearic acid goes to the interface; the area per molecule is found to be 90×10^{-16}, or four and one half times as great as the area occupied by a stearic acid molecule in a condensed film on a free surface of water. If the drop of petrolatum containing stearic acid is allowed to spread on water which already has a film of stearic acid on it held under slight compression, the drop spreads to a considerably smaller area. Such experiments prove that the interfacial film has the properties of a two-dimensional gas which has an equation of state

$$F(a-a_0) = kT, \tag{5}$$

in which the constant k has the same value as it does in Eq. (3) and a_0 has the value 57×10^{-16}. Such a correction to the equation of state for an ideal gas is exactly analogous to the correction in the equation of state for three-dimensional gases when allowance is made for the volume that is occupied by the molecules.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

If now we increase the concentration of the stearic acid in the petrolatum still more so as to have a few parts per thousand instead of per hundred thousand, the drop of the solution when placed on the alkaline water spreads almost instantaneously to a film so thin that iridescent colors appear which are formed by the interference of light reflected from the upper and lower surfaces of the thin layer of oil. These colored films are very convenient to work with, for the color enables us to determine accurately the thickness t; so that, if we have solutions of known concentration n (molecules per cm^3), we can calculate a by the equation

$$a = 1/nt. \tag{6}$$

The method of finding the thickness of the film from the color consists in matching the color of the film against that of a *comparison film*. A *comparison oil* was first made by oxidizing a white mineral oil, or even a lubricating oil, by heating it in an open dish on a hot plate until it smokes. During this process drops of oil are removed from time to time and placed upon a clean water surface. At first the drops form lenses. As oxidation proceeds the lenses spread out into colored films. The oxidation is continued until the films become so thin that the color nearly disappears. A drop of known volume (from a calibrated pipette) is then placed on water in a large tray. By moving a barrier the area of this oil film can be decreased and therefore its thickness can be increased and as this is done the color changes from the original faint yellow to a series of other colors. In this way the color can be brought to match that of any other colored film whose thickness it is desired to measure. This method furnishes us with an extremely accurate and rapid method of measuring a, the area per molecule.

If the water upon which the oil globule is allowed to spread is acid instead of alkaline, the results are strikingly different. No spreading occurs at 25°C unless the concentration of stearic acid in the petrolatum exceeds 0.0032 parts by weight. For concentrations above this, however, the area to which the drop spreads increases linearly and very rapidly with the amount of the stearic acid in the drop. The rate of increase of this area with this concentration enables us to calculate the area per molecule by the equation

$$a = 1/(n-n_0)t, \tag{7}$$

where n_0 is the critical concentration which is just sufficient to cause spreading.

With water that is fairly strongly acid, at temperatures above about 25°C, the area per molecule is found to be 53×10^{-16} cm^2, which is only a little more than half that observed with alkaline water. Measurements made with different external pressures applied to the film prove that this film is also gaseous and has an equation of state given by Eq. (5) with the value $a_0 = 20\times10^{-16}$.

The fact that a certain critical concentration n_0 is necessary on acid water before spreading begins indicates that the two-dimensional gas film at the interface is soluble to some extent in the petrolatum. We have here a case where the inhabitants of Flatland have learned to travel out into three dimensions.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

As long as they remain in Flatland they behave as a perfectly normal two-dimensional gas, but when they are crowded too much they escape into the third dimension and thus show an entirely different behavior.

On acid water at a lower temperature than a certain critical temperature of about 20°C the interfacial film of stearic acid condenses to a two-dimensional liquid, so that the area per molecule suddenly drops from 53 to 20. Very striking color changes are thus often produced by a change of a few tenths of a degree in the temperature of the water on which the oil is allowed to spread. This temperature thus corresponds to the boiling point of a two-dimensional liquid.

A comparison of these results with acid water and with water made alkaline with potassium hydroxide proves that the adsorbed molecules at the interface of alkaline water consist of molecules of soap, that is, of potassium stearate; whereas on acid water they consist of molecules of stearic acid. The large increase in a_0 from 20 to 57 units proves that the soap molecules surround themselves with a single layer of tightly bound water molecules; in other words, become hydrated; but this does not occur with stearic acid molecules.

Recently C. N. Moore and I have been investigating the intermediate field between acid and alkaline water, using solutions that are either neutral or very slightly acid or alkaline. We have also studied the effects of small amounts of calcium, magnesium, sodium and potassium salts in water. We find that in solutions which approximate closely to sea water in composition particularly interesting phenomena are observed. The area per molecule a and the value of n_0 which correspond to the solubility of the film are so remarkably sensitive to slight changes in acidity and alkalinity that the carbon dioxide of the air, which amounts to only a few hundredths of one per cent, produces great changes in these quantities. Sodium and potassium salts greatly increase the area per molecule and so make the film gaseous, whereas calcium and magnesium tend to bring this area down to 20 units and make the films solid. Calcium and sodium thus have an antagonistic action on the properties of these films.

The biologist has found that the permeability of the walls of the cells and many other properties are enormously affected by the ratio of the concentrations of calcium and sodium salts in the surrounding medium.

We are thus led to believe that interfacial films formed between a hydrocarbon which contains stearic acid and an underlying aqueous solution have properties which are in many respects very similar to those of a cell wall. In these experiments we have the advantage, however, that we can make this artificial cell wall cover a square foot if desired; we can study in detail properties which would be very difficult to measure on a living cell. By a quantitative studies we can derive fundamental laws that govern these changes in properties. We hope by following up this work we shall be able to establish some principles that will be of great use to the biologist in understanding the complicated dependence of living cells upon the composition of the surrounding medium.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

SURFACE ELECTRIFICATION DUE TO THE RECESSION OF AQUEOUS SOLUTIONS FROM HYDROPHOBIC SURFACES

Journal of the American Chemical Society
Vol. LX, No. 5, 1190, May (1938).

PORTER and Wyman[1] have shown that calcium stearate multilayers of X-type deposited on a metallic plate give contact potentials of about 70 mv per layer. Thus with a film of 100 layers there is a potential difference of about 7 v in the air between a point just above the stearate layer and another point in the air close to the bare metal surface. This potential in the air, which Porter and Wyman have measured, suggests that there is an internal polarization in the film.

If the plate bearing the film is immersed in water, the external field is short circuited by the water because of its relatively high conductivity and thus a current flows through the water until surface charges have been delivered to the film and the underlying metal which are sufficient to compensate for the original polarization.

Since the plate after being withdrawn from the water possesses the same contact potential as before dipping, it must follow that the act of withdrawal restores the original electric condition of the surface.

A contact potential such as that observed by Porter and Wyman may be due to one or more of the three following factors:

1. *Internal Dipoles.*—If the film is built up of layers of polar molecules all oriented in one direction, there should be a definite number of fixed dipoles per unit volume. Let m be the dipole moment per unit volume. If t is the thickness of the film, and D is the dielectric constant, the effect of the dipoles is to cause an apparent contact potential V equal to

$$V = (4\pi/D) \int m\,dt \qquad (1)$$

Besides the fixed dipoles there may be dipoles which are free to turn in any direction and which contribute to the dielectric constant, as considered in the Debye theory.

---

[1] E. F. Porter and J. Wyman, Jr., *J. Am. Chem. Soc.* **59**, 2746 (1937).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

2. *Surface Charges.*—A surface charge of σ elementary charges $(+e)$ per unit area on the outside layer of a built-up film, together with the corresponding induced surface charge $(-\sigma e)$ at the surface of the underlying metal, gives an apparent contact potential of

$$V = 4\pi\sigma et/D \tag{2}$$

3. *Internal Surface or Volume Charges.*—During the building process, surface charges may be covered by subsequent layers so that internal charges are built into the film. Under the influence of intense fields a redistribution of these charges throughout the volume of the film may occur. It is also possible that if the films are subjected to an intense field sufficient conductivity of the film will occur to carry surface charges into the interior. The potential which results from such internal charges may be calculated by the Poisson equation.

Let us examine the experimental data of Porter and Wyman, including those given in their second paper,[2] to determine the relative importance of these three factors in their contributions to the contact potential.

If we assume that the observed polarization is due to the presence of internal dipoles, there would be no free surface charge with the film in air, but when the plate is immersed in water, there would have to be a surface charge σe sufficient to neutralize the external field. If this field is to reappear when the plate is taken out of the water, it is necessary that this surface charge σe shall be removed from the surface by the act of withdrawing the plate. This could not occur if the plate were hydrophilic, for it would then be covered with a relatively thick film of water, the charge being bound at the interface between the water and the multilayer. If, however, the surface is hydrophobic so that it sheds water and comes out dry, there is a definite line of contact between the water and the film along which the recession of the water from the film takes place. This line of contact can have a width of only a few Ångströms so that, with a surface tension of the order of 40 dynes/cm, the intensity of the force corresponds to a pressure of about 1000 atmospheres.

When the film is under water some of the ions, particularly the polyvalent ones, may be adsorbed by the film. As the contact line passes over the surface of the film, some of these adsorbed ions may remain attached to the film, thus producing a surface charge σe, or the ions may be torn away from the surface by the strong forces and so pass into the water phase. The high dielectric constant of the water would suggest that normally relatively few ions remain on a hydrocarbon surface. If the surface charge is removed in this way the external field due to the internal dipoles reappears when the plate is withdrawn from the water. The recession of the water boundary from the hydrophobic surface is essential for the restoration of the contact potential.

---

[2] E. F. Porter and J. Wyman, Jr., *J. Am. Chem. Soc.* **60**, 1083 (1938).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

On the basis of the foregoing hypothesis, the differences between the X-and the Y-films should be due to the presence of dipoles in the X-films and their absence in the Y-films. In this case the total potential in any film built of X- and Y-films should according to Eq. (1) be proportional to the number of X-layers and independent of the number of Y-layers.

Porter and Wyman in their second paper show that the total potential of a composite film is brought nearly to zero by the addition of one or two pairs of Y-layers, whereas a very few X- layers raise the potential to nearly as high a value as if the whole film were built of X-layers, giving potentials which are approximately proportional to the total thickness of the film, regardless of the relative numbers of X- and Y-layers. This unexpected result seems to indicate that the major cause of the observed contact potential is a surface electrification produced by withdrawing the film from water.

Let us assume that we have a film which contains no internal dipoles but which acquires a surface charge σe on being withdrawn from water. It is evident then from Eq. (2) that the contact potential will increase in proportion to the number of layers.

The surface charge σe depends only upon the nature of the last layer which is deposited and upon the composition of the water, for example, on the pH and presence of certain cations, but not upon the composition of the internal layers.

The observations of Porter and Wyman are thus consistent with the hypothesis that the Y-films are uncharged when they come out of the water, while the X-films carry a positive charge sufficient to give an apparent polarization of 70 mv/layer; which, according to Eq. (2), taking $D = 2.56$, corresponds to $\sigma = 4 \times 10^{11}+$ions per sq., cm, or only 1 ion for every 1200 stearic acid molecules in the surface.

This difference between the X- and Y-films seems to be primarily due to the fact that the X-films are deposited from a solution of pH 9.5, while the Y-films are built from a solution of pH 7.

During the building of X-films there is the possibility of the developments of a surface charge as a kind of frictional electrification, resulting from the slipping of the water surface, with its stearate monolayer, past the film on the plate while this is being withdrawn from the water during the up-trip (no film is deposited during this up-trip). When Y-layers are formed, the up-trip brings the two hydrophilic surfaces of the A- and B-layers together and the water is expelled by cohesive forces between these surfaces, but there is no slipping of one layer past another. Thus it would seem that conditions do not favor the formation of surface charges on Y-layers.

Dr. F. J. Norton, of this Laboratory, has repeated many of Porter and Wyman's experiments and has also studied the effect of dipping X- and Y-films into water containing various salts at different pH's. These experiments also indicate that the composition of the solution is apparently a far more

Digitized by Google Original from UNIVERSITY OF MICHIGAN

important factor in determining the value of σ than is the nature of the outside deposited layer.

Dr. Blodgett recently has found that lead stearate X-films can be built at pH 5.8. These give no contact potentials that increase with the number of layers. This supports the conclusion that it is the pH of the solution rather than the peculiar properties of X-films that gives high potentials. We have found no case in which Y-layers give potentials increasing with the number of layers.

If a film is rendered hydrophilic by dipping into a solution of aluminium chloride or thorium nitrate, it loses all surface charge, regardless of its previous condition. The progressive differences in the contact potential caused by repeated dippings into water solutions are apparently due to partial skeletonization of the film by the removal of stearic acid, thus modifying the surface so that the tendency to pick up ions from the water is changed.

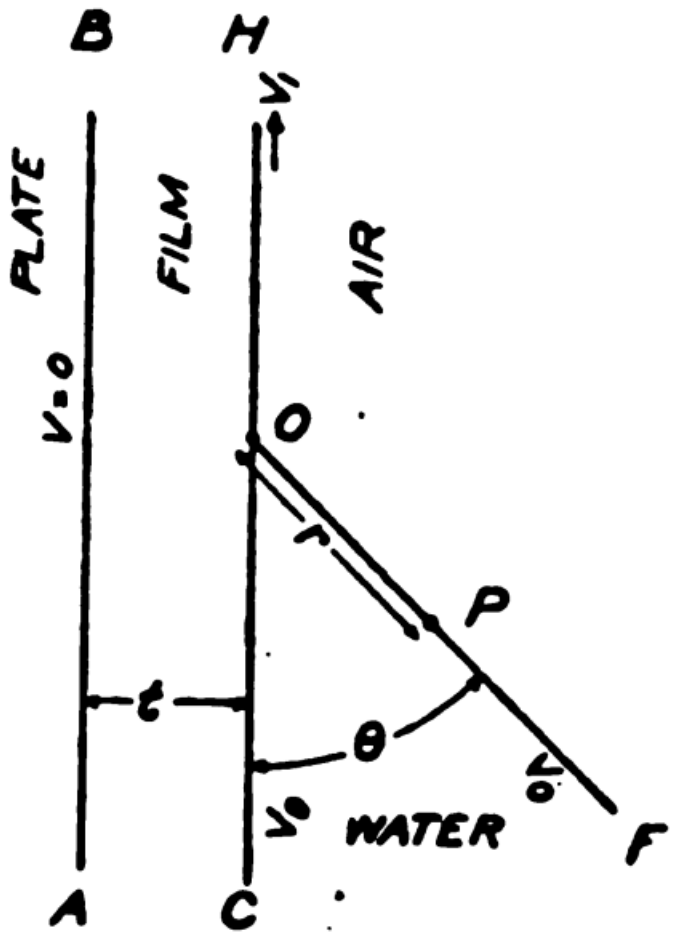


FIG. 1.

By applying potentials of a few volts between the plate and the metallic tray during the deposition of stearate monolyers, it has been found possible to alter the surface charge σe on X- or Y-films and to obtain either positive or negative values of σe over wide ranges in pH.

Dr. Norton also has applied surface charges to stearate films on metal by ionizing the air above the film by means of polonium and by applying various potentials. He is able in this way to charge the films to voltages of about 0.9 v/layer. With more intense fields currents can be made to pass through the films. It is planned to investigate the effect of such currents in producing volume charges within the film. We believe that internal charges can be recognized by time-lag effects like those of the residual charges

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

in Leyden jars. Secondary effects associated with redistributions of internal charges are probably responsible for some of the phenomena observed by Porter and Wyman which indicate departure from the simple theory of surface charges which is here proposed as an explanation of the main features of the phenomena.

The surface charge σe left on the X-films after each up-trip must theoretically modify the contact angle θ and must produce electric fields parallel to the surface which tend to limit the development of the charge.

Let BA in Fig. 1 represent the cross section of the surface of a metallic plate on which there is a deposited film of thickness t whose other surface is CH_0. Consider that the plate is being raised out of water which gives a contact angle θ against the film. Thus OC is the film-water interface, OF the water-air interface, and OH the film-air interface on which a positive surface charge σe is left by the receding water.

Let the potential of the metallic plate be zero and V_0 be the potential of the water along OC and OF.

The potential on the surface OH increases from V_0 at O toward a limiting value V_1 at distances from O which are large compared to t. Here

$$V_1 = 4\pi\sigma et/D \tag{3}$$

By means of a Schwartz-Christoffel transformation it is possible when $D = 1$ to calculate the potential distribution in terms of an auxiliary complex variable η. The electric field at the surface OF is perpendicular to OF and is of an intensity E given by[3]

$$E = D(Vs - V_1)/t\eta^{\alpha} \tag{4}$$

where

$$\alpha = (\pi - \theta)/\pi \tag{5}$$

θ being expressed in radians. On the surface OF, η is real and is defined by

$$r = (t/\pi D)\int_0^{\eta} \eta^{\alpha} d\eta/(1+\eta) \tag{6}$$

where r is the distance of the point P, on the surface OF, from the contact line represented by O. For values $\eta \ll 1$ the relation between r and η is given approximately by

$$r = (t/D\pi)\eta^2[\ln(1+\eta) - \alpha\eta_1(1+\alpha) + \alpha\eta^2/4(1+\alpha/2) -] \tag{7}$$

At large distances, $\eta \gg 1$, we have

$$r = (t/D\pi)\eta^{\alpha}[(1/\alpha) + \ln(1+1/\eta) + \alpha/\eta - \alpha/4\eta^2 +] - (t/DR)[(1/\alpha) + \alpha\pi^2/6] \tag{8}$$

---

[3] The treatment as given is rigorous only when $D = 1$, but should give a reasonably good approximation for $D = 1$. The assumption has been made that the effect of the dielectric constant is equivalent to a change in thickness, thus t in the original equation has been replaced by t/D.

Digitized by Google Original from UNIVERSITY OF MICHIGAN

The field E exerts a pressure $-E^2/8\pi$ on the water surface OF whose integral from $r = 0$ to $r = \infty$ (per cm of length of contact line) is

$$F = (1/8\pi)\int_0^\infty E^2\,\mathrm{d}r = D(Vs-V_2)^2G/8\pi^2ta(1-a) \tag{9}$$

where G is a function of a that varies only between the limits of 1.00 (at $a = 0$ and at $a = 1$) and 0.785 (at $a = 1/2$) and is expressed in terms of gamma functions by

$$G = \mathrm{T}(1+a)\cdot\mathrm{T}(2-a) \tag{10}$$

The "force" F has the dimensions of a surface tension, dynes/cm, and its effect is to decrease the contact angle Θ by an amount

$$\Delta\Theta = F/\gamma \tag{11}$$

where γ is the surface tension of the water surface DF. The work of adhesion W ordinarily given by

$$\Delta W = \gamma(1+\cos\Theta) \tag{12}$$

is increased by an amount

$$W = F\sin\Theta \tag{13}$$

Very close to the contact line O the field E can be obtained by eliminating η from Eqs. (4) and (7), taking only first order terms

$$E = [D(V_0-V_1)/t](t/D\pi r)^{a/(1+a)} \tag{14}$$

Let us apply these equations to an X-film of N layers which give a contact potential of 70 mv/layer. We take $D = 2.56$; $V_0 = 0$; $V_1 = 0.070\ N$ volt cm^{-1}, and $t/N = 24.4\times10^{-8}$ cm as found for barium stearate films in this Laboratory, and obtain

$$E = 7.3\times10^5(3.03\times10^{-3}N/r)^{a/(1+a)}\,v/\mathrm{cm} \tag{15}$$

and, if $G = 0.8$

$$F = 0.006N/a(1-a)\,\mathrm{dynes/cm}. \tag{16}$$

If the contact angle $\Theta = 90°$ (about right for X-films), $a = 0.5$ and thus E varies in inverse proportion to the cube root of r and reaches values of 10^6 v/cm when $r = 1.2\times10^{-3}N$. Thus with 50 layers the field of 10^6 v/cm would extend to a distance of 60 Å, while at a distance of 6 Å the field would be 2.15×10^6 v/cm, a not unreasonably large value. If, however. we should build a film of 500 layers, the field at $r = 6$ Å would be 4.6×10^6 v/cm, There should thus be some limiting thickness of film beyond which the contact potential no longer increases in proportion to N. Porter and Wyman's data seem to show such a limit at about 200 layers.

By Eqs. (16) and (11), taking $\gamma = 40$ dvnes/cm (for a monolayer under oleic acid pressure), the change of contact angle should be $\Theta = 0.35\ N$ degrees. Thus up to $N = 100$ the change in contact angle would be only

Digitized by Google Original from UNIVERSITY OF MICHIGAN

3.5° and would be unnoticeable, but with several hundred layers the surface would tend to become hydrophilic and the surface charge could no longer be found

The author is obligated to Dr. H. Poritsky for an outline of the method used for calculating the potential distribution illustrated in Fig. 1.

Summary

The progressively increasing contact potentials observed by Porter and Wyman during the building up of calcium stearate multilayers of type X on alkaline solutions seem to be due to a surface charge on the uppermost monolayer rather than to the presence of dipole molecules within the film. A theory is given for the potential distribution produced by these surface charges and it is shown that with potential gradients of the order of 3×10^6 v/cm over distances of a few Ångström units the contact potentials can increase at a linear rate of 70 mv per layer only up to films of a thickness of a few hundred layers.

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

REPULSIVE FORCES BETWEEN CHARGED SURFACES IN WATER, AND THE CAUSE OF THE JONES-RAY EFFECT

Science
Vol. LXXXVIII, No. 2288, 430, November (1938).

CONSIDER a plane surface of potential V which bounds a semi-infinite volume of a dilute salt solution of potential 0. Taking the salt to be of the univalent type, such as KCl and applying the Poisson and Boltzmann equations, the potential distribution must satisfy the equation

$$\frac{d^2V}{dx^2} = 4\pi n_0(e/D)\,[\exp(Ve/kT) - \exp(-Ve/kT)], \tag{1}$$

where n_0 is the number of ions (of each sign) per unit volume in the solution in regions where $V = 0$.

Let us put

$$\eta = Ve/kT \tag{2}$$

and

$$\theta = x/\lambda \tag{3}$$

where λ, the value of $1/\kappa$ in the Debye-Hückel theory, is given by

$$\lambda^2 = DkT/8\pi e^2 n_0 \tag{4}$$

Eq. (1) then becomes

$$2d^2\eta/d\theta^2 = \varepsilon^{\eta} - \varepsilon^{-\eta} \tag{5}$$

In the Debye-Hückel theory it is assumed that η is so small that ε^{η} can be replaced by $1+\eta$. We wish, however, to apply Eq. (5) to two parallel plates which are separated by the distance b but are so close together and are so highly positively charged that $\eta > 1$, everywhere between the plates. The Debye-Hückel approximation therefore can not be used, but instead, we can neglect $\varepsilon^{-\eta}$ in Eq. (5), since it is small compared to ε^{η}.

Integration gives

$$\theta = 2\exp(-\eta_M/2)\tan^{-1}[\exp(\eta-\eta_M)-1]^{1/2}. \tag{6}$$

where η_M is the minimum value of η which occurs at the plane half way between the plates and θ measures the distance from this median plane. If η_1 and θ_1 are the values of η and θ at the surface of the plates and we take the case that the plates are so highly charged that $\eta_1 > \eta_M$ then Eq. (6). becomes

$$\theta_1 = \pi\exp(-\eta_M/2) - 2\exp(-\eta_1/2) \tag{7}$$

where the term containing η_1 is very small compared to that which contains η_M.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Repulsive Forces Between Plates.—The plates are acted upon by forces of two kinds: A pressure nkT due to the negative ions and a negative pressure or pull due to electric field E; the sum of the two must be constant for all values of θ in the space between the plates. At the median plane we see from the symmetry that $E = 0$ and therefore the force acting per unit area on the plates is the pressure $p = n_M kT$ where n_M is the concentration of negative ions at the median plane.

The value of n_M can be calculated from η_M by the Boltzmann equation. To obtain the net pressure between the plates we should subtract the pressure $2n_0kT$ which acts on the other side of each plate, giving

$$p = n_0 kT(\exp \eta_M - 2) \tag{8}$$

Since, however, we are taking at present only the case where $\eta s > \eta_M > 1$ we can neglect the 2 in the parenthesis in Eq. (8) and the last term of Eq. (7) and so from Eqs. (7), (8) and (3), placing $x_1 = b/2$, we obtain

$$p = n_0 kT(2\pi\lambda/b)^2 \tag{9}$$

We can now eliminate λ by Eq. (4):

$$p = (\pi/2) D(kT/eb)^2 \tag{10}$$

This gives the repulsive force between two planes with high charges of similar sign when they are separated by a distance which is small compared to 2λ. It is interesting to note that this limiting expression does not contain the potential of the plates, the concentration of the electrolyte or any other adjustable parameter. The force varies inversely as the square of the distance between the plates. To determine its numerical magnitude let us place $D = 81$ (the dielectric constant of water at 20°C), $T = 293$°K and so obtain

$$p = 8.90 \times 10^{-7}/b^2 \text{ dynes/cm}^2 \tag{11}$$

Thus, when the surfaces are at a distance of 10^{-4} cm (1μ) the repulsive force is 89 dynes cm^{-2}.

This repulsive force, which involves no new mechanism, together with attractive Coulomb forces, is found to be of just the right magnitude to account for the formation of tactoids and unipolar coacervates (which involve the spontaneous separation of certain colloidal solutions into two liquid phases).[1]

Repulsion Between a Plate and an Air-Water Interface.—The same pressure p, which acts according to Eq. (10) between two plates separated by the distance b, should also act between a single plate and an air-water interface at a distance $b/2$, for in both cases at a distance $b/2$ from the plate the boundary condition $d\eta/d\theta = 0$ is fulfilled. If then a highly charged (ζ-potential) plate held vertically is partly raised out of a dilute water solution of an electrolyte, the water should drain off until a limiting thickness t is reached, where t

[1] A paper soon to appear in the *Journal of Chemical Physics.*

Digitized by Google Original from UNIVERSITY OF MICHIGAN

will vary with the height h above the water surface. In the liquid of the film when equilibrium has been reached there will be a pressure

$$p = -\varrho g h \tag{12}$$

if the pressure at the free horizontal surface is zero. Here ϱ is the density and g the acceleration of gravity.

The surface of the water film is acted on by this negative pressure and by the positive outward pressure p given by Eq. (10), and these two forces must be equal. Eliminating p between Eqs. (10) and (12), we find that the film thickness is

$$t = (kT/e)(\pi D/8\varrho g h)^{1/2} = 1.52\times 10^{-5}/h^{12} \text{ cm} \tag{13}$$

if we take $D = 81$, $T = 293°\text{K}$, $\varrho = 1$, $g = 980$. Thus at a height of 10 cm above the horizontal water surface the film of water should have a thickness of 480 Å.

Experiments are under way to measure the thickness of such films on barium stearate multilayers of critical thickness, which have been made hydrophilic by conditioning in thorium nitrate and sodium silicate. Because of the negative pressure in the water in these films, the vapor pressure of the water must be lowered, but calculation shows that an elevation of temperature of only 0.001°C would decrease t from 480 Å to 165 Å. To obtain data for a quantitative test of Eq. (13) it will be necessary to have good temperature control.

Water Films on the Walls of Capillaries.—In a capillary tube of radius r in presence of saturated water vapor, there will also be a water film.

Because of the curvature (one half that of a sphere of equal radius) the surface tension γ exerts a force or pressure γ/r on the surface of the film that acts in the same direction as that given by Eq. (10). Thus in place of Eq. (13) we have

$$\Delta r = (kT/e)[\pi D/8(\varrho g h - \gamma/r)]^{1/2} \tag{14}$$

Surface Tensions of Dilute Salt Solutions.—Jones and Ray,[2] by developing an extremely accurate differential method for measuring relative surface tensions, have found an extraordinary effect by which very low concentrations of salts appear to *decrease* the surface tension of water. The effect occurs only at molar concentrations (of KCl) below about 8×10^{-4} and the maximum decrease amounts to about 0.015 dyne cm^{-1}.

The theory outlined above which led to Eq. (14) seems to offer a simple explanation of the Jones-Ray effect. A water film on the wall of the capillary has the effect of decreasing the effective radius so that the solution rises to a greater height than if such a film were not present. The film disappears at higher salt concentrations because the charge (ζ-potential) be-

[2] Grinnell Jones and W. A. Ray, *J. Am. Chem. Soc.* 59:187, 1937.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

comes less (or λ becomes comparable to Δr), and thus the capillary rise h_s decreases and produces an apparent decrease in surface tension.

If we measure the capillary rise in a tube of radius r whose walls are covered by a water film of thickness Δr the surface tension of the water should be calculated by

$$\gamma = \frac{1}{2}\varrho g h(r-\Delta r). \tag{15}$$

Jones and Ray, however, calculated their surface tension by the equation

$$\gamma_{JR} = \frac{1}{2}\varrho g h r. \tag{16}$$

The value of Δr can be calculated by Eq. (14) by inserting $\gamma/r = \varrho g h/2$, so that we have

$$\Delta r = (kT/2e)(\pi D/\varrho g h)^{1/2} = 2.16\times 10^{-5}/h^{1/2} \tag{17}$$

According to this interpretation the values of γ_{JR} at low concentrations are higher than the true surface tension of water by an amount:

$$\gamma_{JR}-\gamma = (kT/4e)(\pi D\varrho g h)^{1/2} = 0.0107h^{1/2} \tag{18}$$

Jones and Ray in all their experiments used a single capillary of radius $r = 0.01361$ cm, and the capillary rise was $h = 10.8$ cm. According to Eq. (18) the increment $\gamma_{JR}-\gamma$ should have been 0.035 dyne cm^{-1}. This is of the same order of magnitude as the apparent decrease in surface tension of 0.015 dyne cm^{-1} which they observed at concentrations below 10^{-3} M.

The values of Δr and $\Delta\gamma$ given by Eqs. (17) and (18) have been based on the assumptions that $\Delta r << \lambda$ and $\eta_1 >> \eta_M >> 1$. When these conditions are not fulfilled, Δr and $\Delta\gamma$ will have lower values.

In the following table the values of λ are given for various assumed concentrations between 10^{-3} and 10^{-5} M as calculated from Eq. (4). The next column contains values of $\Delta\gamma$ from a curve plotted from data of Jones and Ray for KCl. From these we can calculate values of Δr which would account for these values of $\Delta\gamma$. The last column gives η_M as calculated from Eq. (8) by inserting $p = \varrho g h/2 = 5300$ dynes cm^{-2}. The values of λ decrease far below the maximum value of Δr (280 Å), but Δr decreases too, so that in all cases the condition $\Delta r << \lambda$ is approximately fulfilled. The reason that Δr never rises as high as 650 Å, which is given by Eq. (17), is that the condition $\eta_1 >> \eta_M$ is not fulfilled at the lowest concentrations.

The ζ-potentials determined by the electric mobility of particles of glass and quartz[3] are negative and are of the order of 50 to 100 millivolts at concentrations of about 10^{-5} to 10^{-6} M and decrease rapidly as the concentration rises from 10^{-4} to 10^{-3} M. The highest values of η_1 calculated by Eq. (2) from these potentials thus range from 2 to 4. The marked decrease in η_M to low values

[3] H. A. Abramson, *Electrokinetic Phenomena*, Chemical Catalog Company, New York, 1934. See pp. 203–8.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

TABLE I

Calculations Based on the Surface Tension Data of Jones and Ray for KCl

Molar concentration	λ	$\gamma_{JR}-\gamma$ dyne cm^{-1}	Δr obs	η_M
0.0010	97 Å	0.000	..	0.46
0.0005	137	0.0014	26 Å	0.65
0.0003	178	0.0065	122	0.82
0.0002	217	0.009	174	1.01
0.0001	307	0.012	230	1.36
10^{-4}	970	0.015	280	3.15

shown in Table I as the concentration increases is probably the cause of the decreases in Δr and $\Delta\gamma$ at higher concentrations.

These rough calculations show that the Jones-Ray effect can be adequately explained on the basis of a water film held on the surface of the capillary tube by electric charges bound by the quartz.

The present paper is merely preliminary. It has been possible to obtain a complete integration of Eq. (5) in terms of elliptic functions. Some calculations have shown that by applying these exact expressions to the experimental data of Jones and Ray it is possible to calculate the potential of the quartz surface at each concentration. These potentials are reasonable and vary with the concentration in the manner shown by mobility experiments.

Further experiments should make it possible to check this suggested theory. For example, we see by Eq. (18) that $\Delta\gamma$, which does not represent a true change in surface tension, should vary in proportion to $h^{1/6}$ or $r^{-1/6}$. The addition of thorium nitrate in concentration of 10^{-6} M brings the ζ-potential of glass to about zero.[3] This should eliminate the Jones-Ray effect. If solutions of proteins are passed through the capillary and this is then carefully washed, the ζ-potential can be made to vary through wide ranges, depending on the choice of protein, and the pH of the solution. This should cause marked variations in the Jones-Ray effect.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

APPENDIX I

Irving Langmuir — Curriculum Vitae

Born

January 31, 1881

Parents

Charles and Sadie Comings Langmuir

Attended

Public Schools, Brooklyn	1887—1892
Boarding School, Suburban Paris	1892—1895
Chestnut Hill Academy, Philadelphia	1895—1896

Graduated

Manual Training High School, Pratt Institute	1898

Received degree

Metallurgical Engineer, Columbia University	1903
Doctor of Philosophy, University of Göttingen	1906

Taught

Stevens Institute of Technology	1906—1909

Married

Marian Mersereau	1912

Children

Son, Kenneth

Daughter, Mrs. H. R. Summerhayes

Research Scientist

General Electric Research Laboratory	1909—1950
Associate Director	1929—1950
Consultant	1950—1957

Honorary Degrees Awarded

D.Sc. Northwestern University	1921
LL.D. Edinburgh University	1921
D.Sc. Union University	1923
D.Sc. Columbia University	1925
D.Sc. Kenyon College	1927
D.Sc. Princeton University	1929
D.Ing. Tech. Hochschule, Berlin	1929
D.Sc. Lehigh University	1934

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

	LL.D. Union University	1934
	LL.D. Johns Hopkins University	1936
	D.Sc. Harvard University	1938
	D.Sc. Oxford University	1938
	D.Sc. Rutgers University	1941
	D.Sc. Queen's College (Canada)	1941
	LL.D. University of California	1946

Medals Awarded

Nichols Medal	American Chemical Society	1915
Hughes Medal	Royal Society of London	1918
Rumford Medal	American Association for the Advancement of Science	1920
Nichols Medal	American Chemical Society	1920
Stanislao Cannizzaro Award	Royal National Academy of Linnaeus (Rome)	1925
Perkins Medal	Society Chemical Industry (American Section)	1928
Chandler Medal	Columbia University	1929
Willard Gibbs Medal	American Chemical Society	1930
NOBEL PRIZE	Swedish Academy	1932
Popular Science	Popular Science Monthly	1933
Franklin Medal	Franklin Institute	1934
Holley Medal	American Society of Mechanical Engineers	1934
John Scott Medal	Philadelphia Board of Directors of City Trusts	1937
Faraday Medal	Chemical Society (London)	1938
Egleston Medal	Columbia University Engineering Schools Alumni Association	1939
Modern Pioneer of Industry	National Association of Manufacturers	1940
Silver Beaver	Boy Scouts of America	1942
Faraday Medal	Institution of Electrical Engineers	1943
Medal of Merit	United States Army and Navy	1948
Mascart Medal	Academy des Sciences, Societé Française des Electriciens	1948
John J. Carty Medal	National Academy of Sciences	1949
Silver Buffalo	Boy Scouts of America	1950

Died

August 16, 1957

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

APPENDIX II

COMPLETE LIST OF PAPERS OF DR. IRVING LANGMUIR AS THEY APPEAR IN THE LANGMUIR MEMORIAL VOLUMES*

VOLUME 1

LOW-PRESSURE PHENOMENA

Mechanism of Chemical Reactions

1. The Partial Recombination of Dissociated Gases During Cooling. Inaugural dissertation for Doctor's Degree, Göttingen. (1906).
2. The Dissociation of Water Vapor and Carbon Dioxide at High Temperatures. JACS, **28**, 1357 (1906).
3. The Velocity of Reactions in Gases Moving Through Heated Vessels and the Effect of Convection and Diffusion. JACS, **30**, 1742 (1908).
8. A Chemically Active Modification of Hydrogen. JACS, **34**, 1310 (1912).
7. The Dissociation of Hydrogen into Atoms. JACS, **34**, 860 (1912).
18. Note on the Heat of Formation of Hydrogen from Hydrogen Atoms. Phil. Mag., **27**, 188 (1914).
22. The Dissociation of Hydrogen into Atoms. (With G. M. J. Mackay). JACS, **36**, 1708 (1914).
25. The Dissociation of Hydrogen into Atoms. II. Calculation of the Degree of Dissociation and the Heat of Formation. JACS, **37**, 417 (1915); Zeit. f. Electrochemie, **23**, 217 (1917).
37. Dissociation of Hydrogen into Atoms. III. JACS, **38**, 1145 (1916).
9. Chemical Reactions at Very Low Pressures. I. The Clean-up of Oxygen in a Tungsten Lamp. JACS, **35**, 105 (1913).
13. Chemical Reactions at Very Low Pressures. II. The Chemical Clean-up of Nitrogen in a Tungsten Lamp. JACS, **35**, 931 (1913).
27. Chemical Reactions at Low Pressures. JACS, **37**, 1139 (1915).
52. Chemical Reactions at Low Pressures. IV. The Clean-up of Nitrogen by a Heated Molybdenum Filament. JACS, **41**, 167 (1919).
66. Radiation as a Factor in Chemical Action. JACS, **42**, 2190 (1920).

---

* Editor's Note: The numbers represent the order in which the papers were published.

Digitized by Google

Original from UNIVERSITY OF MICHIGAN

72. Chemical Reaction on Surfaces. G. E. Rev., **25**, 445 (1922); Trans. Faraday Soc., **17**, 607 (1921).
73. The Mechanism of the Catalytic Action of Platinum in the Reactions $2CO + O_2 = 2CO_2$ and $2H_2 + O_2 = 2HO$. Trans. Faraday Soc., **17**, 621 (1921).

VOLUME 2

Heat Transfer — Incandescent Tungsten

Part 1 — *Transfer of Heat*

4. Thermal Conduction and Convection in Gases at Extremely High Temperatures. Trans. Amer. Electrochem. Soc., **20**, 225 (1911).
5. Convection and Conduction of Heat in Gases. Phys. Rev., **34**, 401 (1912).
6. Convection and Conduction of Heat in Gases. Proc. AIEE, **31**, 1011 (1912).
10. Laws of Heat Transmission in Electrical Machinery. Proc. AIEE, **32**, 391 (1913).
11. Convection and Radiation of Heat. Trans. Amer. Electrochem. Soc., **23**, 299 (1913).
12. Flow of Heat Through Furnace Walls: the Shape Factor. (With E. Q. Adams and G. S. Meikle). Trans. Amer. Electrochem. Soc., **24**, 53 (1913).
103. Flames of Atomic Hydrogen. Science, **62**, 463 (1925).
104. Flames of Atomic Hydrogen. G. E. Rev., **29**, 153 (1926).
105. Atomic Hydrogen Arc Welding. (With R. A. Weinman). G. E. Rev., **29**, 160 (1926).
110. Flames of Atomic Hydrogen. Ind. and Engrg. Chem., **19**, 667 (1927).

VOLUME 2

Heat Transfer — Incandescent Tungsten

Part 2 — *Incandescent Lamps and Tungsten*

14. Tungsten Lamps of High-efficiency. I. Blackening of Tungsten Lamps and Methods of Preventing it. II. Nitrogen-filled Lamps. (With J. A. Orange). Proc. AIEE, **32**, 1894 (1913); Trans. AIEE, **32**, 1913 (1913); G. E. Rev., **16**, 956 (1913).
20. The Flicker of Incandescent Lamps on Alternating Current Circuits and Stroboscopic Effects. G. E. Rev., **17**, 294 (1914).
26. The Melting Point of Tungsten. Phys. Rev., **6**, 138 (1915).
34. The Characteristics of Tungsten Filaments as Functions of Temperature. Phys. Rev., **7**, 302 (1916).
111. The Characteristics of Tungsten Filaments as Functions of Temperature. (With H. A. Jones). G. E. Rev., **30**, 408; 310; 354 (1927).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

126. Effect of End Losses on the Characteristics of Filaments of Tungsten and other Materials. (With S. MacLane and K. B. Blodgett). Phys. Rev., **35**, 478 (1930).
151. The Design of Tungsten Springs to Hold Tungsten Filaments Taut. (With K. B. Blodgett). Rev. Sci. Instru., **5**, 321 (1934).
156. Radiation and Absorption of Energy by Tungsten Filaments at Low Temperatures. (With J. B. Taylor), Jour. Opt. Soc. Amer., **25**, 321 (1935).
159. The Heat Conductivity of Tungsten and the Cooling Effects of Leads upon Filaments at Low Temperatures. (With J. B. Taylor). Phys. Rev., **50**, 68 (1936).

VOLUME 3

THERMIONIC PHENOMENA

Part 1 — *Thermionics* — *Vacuum Pumps*

17. The Effect of Space Charge and Residual Gases on Thermionic Currents in High Vacuum. Phys. Rev., **2**, 450 (1913).
28. The Pure Electron Discharge and its Applications in Radio Telegraphy and Telephony. G. E. Rev., **18**, 327 (1915); Trans. AIRE, **3**, 261 (1915).
65. Fundamental Phenomena in Electron Tubes Having Tungsten Cathodes. (Part I and Part II). G. E. Rev., **23**, 503, 589 (1920).
79. Use of High-power Vacuum Tubes. Electrical World, **80**, 881 (1922).
81. The Effect of Space Charge and Initial Velocities on the Potential Distribution and Thermionic Current between Parallel Plane Electrodes. Phys. Rev., **21**, 419 (1923).
85. A New Photo-electric Effect Reflection of Electrons Induced by Light. Science, **58**, 398 (1923).
91. Currents Limited by Space Charge between Coaxial Cylinders. (With K. B. Blodgett). Phys. Rev., **22**, 347 (1923).
93. Currents Limited by Space Charge between Concentric Spheres. (With K. B. Blodgett). Phys. Rev. **23**, 49 (1924).
133. Diffusion of Electrons back to an Emitting Electrode in a Gas. Phys. Rev., **38**, 1656 (1931).
33. A New Vacuum Gage of Extreme Sensitiveness. (Abstract). Phys. Rev., **1**, 337 (1913).
38. A High Vacuum Mercury Vapor Pump of Extreme Speed. Phys. Rev., **8**, 48 (1916).
44. The Condensation Pump: an Improved Form of High Vacuum Pump. G. E. Rev., **19**, 1060 (1916); Jour. Franklin Inst., **182**, 719 (1916).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

VOLUME 3

THERMIONIC PHENOMENA

Part 2 — Electron Emission and Adsorbed Films

36. The Relation Between Contact Potentials and Electrochemical Action. Trans. Amer. Electrochem. Soc., **29**, 125 (1916).
80. Thermionic Effects Caused by Alkali Vapors in Vacuum Tubes. (With K. H. Kingdon). Science, **57**, 58 (1923).
83. Removal of Thorium by Positive Ion Bombardment. (With K. H. Kingdon). Phys. Rev., **22**, 148 (1923).
87. Electron Emission From Caesium-covered Filaments. (With K. H. Kingdon). Phys. Rev., **23**, 112 (1923).
90. The Electron Emission From Thoriated Tungsten Filaments. Phys. Rev., **22**, 357 (1923).
100. Thermionic Effects Caused by Vapors of Alkali Metals. (With K. H. Kingdon). Proc. Roy. Soc., A, **107**, 61 (1925).
109. On the Surface Heat of Charging. (With L. Tonks). Phys. Rev., **29**, 524 (1927).
121. Contact Potential Measurements With Adsorbed Films. (With K. H. Kingdon). Phys. Rev., **34**, 129 (1929).
127. Electrochemical Interactions of Tungsten, Thorium, Caesium, and Oxygen. Ind. and Engrg. Chem., **22**, 390 (1930).
129. Oxygen Films on Tungsten. I. A Study of Stability by Means of Electron Emission in Presence of Cesium Vapor. (With D. S. Villars). JACS, **53**, 486 (1931).
130. The Alleged Production of Adsorbed Films on Tungsten by Active Nitrogen. Phys. Rev., **37**, 1006, (1931).
137. Cesium Films on Tungsten. JACS, **54**, 1252 (1932).
139. The Mobility of Caesium Atoms Adsorbed on Tungsten. (With J. B. Taylor). Phys. Rev., **40**, 463 (1932).
144. The Nature of Adsorbed Films of Caesium on Tungsten. I. The Space Charge Sheath and the Image Force. Phys. Rev., **43**, 224 (1933).
145. The Evaporation of Atoms, Ions, and Electrons from Caesium Films on Tungsten. (With J. B. Taylor). Phys. Rev., **44**, 423 (1933).
148. Thoriated Tungsten Filaments. Jour. Franklin Inst., **217**, 543 (1934).
164. Vapor Pressure of Caesium by the Positive Ion Method. (With J. B. Taylor). Phys. Rev., **51**, 753 (1937).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

VOLUME 4

Electrical Discharge

Fundamental Phenomena in Electrical Discharges

82. Positive Ion Currents from the Positive Column of Mercury Arcs. Science, **58**, 290 (1923).
84. Positive Ion Currents from the Positive Column of the Mercury Arc. G. E. Rev., **26**, 731 (1923).
92. A Simple Method for Quantitative Studies of Ionization Phenomena in Gases. Science, **59**, 380 (1924).
97. A New Type of Electric Discharge: the Streamer Discharge. Science, **60**, 392 (1924).
94. 95. 96. 98. 99. Studies of Electric Discharges in Gases at Low Pressures. (With H. Mott-Smith). G. E. Rev., **27**, 449; 538; 616; 762; (1924).
108. The Theory of Collectors in Gaseous Discharges. (With H. Mott-Smith). Phys. Rev., **28**, 727 (1926).
114a. Electric Discharges in Gases at Low Pressures. Estratto Dagli Atti del Congresso Internazionals del Fisici Como (Sept. 1927). English translation.
119. Control of an Arc Discharge by Means of a Grid. (With A. W. Hull). Proc. NAS, **51**, 218 (1929).
141a. Electric Discharges in Gases at Low Pressures. Jour. Franklin Inst., **214**, 275 (1932).
154. Electric Discharges in Vacuum and in Gases at Low Pressures. The Denki-Gakkwai, Iwadare Foundation, Lecture III, Japan (1934).
128. Electrical Discharges in Gases. I. Survey of Fundamental Processes. (With K. T. Compton). Rev. Mod. Phys., **2**, 123 (1930).
132. Electrical Discharges in Gases. II. Fundamental Phenomena in Electrical Discharges. (With K. T. Compton). Rev. Mod. Phys., **3**, 191 (1931).

VOLUME 5

Plasma and Oscillations

Ionized Gases

86. The Pressure Effect and Other Phenomena in Gaseous Discharges. Jour. Franklin Inst., **196**, 751 (1923).
101. Scattering of Electrons in Ionized Gases. Phys. Rev., **26**, 585 (1925).
107. The Flow of Ions Through a Small Orifice in a Charged Plate. (With L. Tonks and H. Mott-Smith). Phys. Rev., **28**, 104 (1926).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

116. Collisions Between Electrons and Gas Molecules. (With H. A. Jones). Phys. Rev., **31**, 357 (1928).
117. Oscillations in Ionized Gases. Proc. NAS, **14**, 627 (1928).
117a. Oscillations in an Ionized Gas. (With L. Tonks). Science, **68**, 598 (1928).
118. Oscillations in Ionized Gases. (With L. Tonks). Phys. Rev., **33**, 195 (1929).
120. The Interaction of Electron and Positive Ion Space Charges in Cathode Sheaths. Phys. Rev., **33**, 954 (1929).
122. General Theory of the Plasma of an Arc. (With L. Tonks). Phys. Rev., **34**, 876 (1929).
128a. Metastable Atoms and Electrons Produced by Resonance Radiation in Neon. (With C. G. Found). Phys. Rev., **36**, 604 (1930).
136. Study of a Neon Discharge by Use of Collectors. (With C. G. Found). Phys. Rev., 39, 237 (1932).

VOLUME 6

Structure of Matter

Part 1 — *Atomic Structure*

59. The Structure of Atoms and the Octet Theory of Valence. Proc. NAS, **5**, 252 (1919).
56. The Arrangement of Electrons in Atoms and Molecules. G. E. Rev. **22**, 505, 587, 789 (1919); JACS, **41**, 868 (1919).
60. The Octet Theory of Valence and its Applications With Special Reference to Organic Nitrogen Compounds. JACS, **42**, 274 (1920).
61. The Structure of Atoms and its Bearing on Chemical Valence. Jour. Ind. and Engrg. Chem., **12**, 386 (1920).
62. The Charge on the Electron and the Value of Planck's Constant **h**. Jour. Franklin Inst., **189**, 603 (1920).
63. Theories of Atomic Structure. Nature, **105**, 261 (1920).
64. The Structure of the Helium Atom. Science, **51**, 604 (1920).
68. The Structure of the Helium Atom. Phys. Rev., **17**, 339 (1921).
69. The Structure of the Static Atom. Science, **53**, 290 (1921).
71. Types of Valence. Science, **54**, 59 (1921).

VOLUME 6

Structure of Matter

Part 2 — *Molecules and Crystalline Structure*

58. Isomorphism, Isosterism, and Covalence. JACS, **41**, 1543 (1919).
64a. The Structures of the Hydrogen Molecule and the Hydrogen Ion. Science, **52**, 433 (1920).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

76. The Diffusion Coefficient in Solids and its Temperature Coefficient. (With S. Dushman). Phys. Rev., **20**, 113 (1922).
102. The Distribution and Orientation of Molecules. Colloid Symposium Monograph, **3**, 48 (1925).
106. The Effects of Molecular Dissymmetry on Properties of Matter. Colloid Chemistry, **1**, 525 (1926).
125. Forces Near the Surfaces of Molecules. Chem. Rev., **6**, 451 (1929).
67. The Crystal Structure of the Ammonium Halides Above and Below the Transition Temperatures. (With Guy Barlett). JACS, **43**, 84 (1921).
184. Vector Maps and Crystal Analysis. (With D. M. Wrinch). Nature, **142**, 581 (1938).
186. The Role of Attractive and Repulsive Forces in the Formation of Tactoids, Thixotropic Gels, Protein Crystals, and Coacervates. Jour. Chem. Phys., **6**, 873 (1938).
134. Regions of Reversed Magnetization in Strained Wires. (With K. J. Sixtus). Phys. Rev., **38**, 2072 (1931).

VOLUME 7

Protein Structures

Molecular Structure

163. Built-up Films of Proteins and Their Properties. (With V. J. Schaefer and D. M. Wrinch). Science, **85**, 76 (1937).
168. Multilayers of Sterols and the Adsorption of Digitonin by Deposited Monolayers. (With V. J. Schaefer and H. Sobotka). JACS, **59**, 1751 (1937).
169. Improved Methods of Conditioning Surfaces for Adsorption. (With V. J. Schaefer). JACS, **59**, 1762 (1937).
170. Monolayers and Multilayers of Chlorophyll. (With V. J. Schaefer). JACS. **59**, 2075 (1937).
177. The Adsorption of Proteins at Oil-water Interfaces and Artificial Protein-lipoid Membranes. (With D. F. Waugh). Jour. Gen. Physio., **21**, 745 (1938).
178. Activities of Urease and Pepsin Monolayers. (With V. J. Schaefer). JACS, **60**, 1351 (1938).
183. Salted-out Protein Films. (With V. J. Schaefer). JACS, **60**, 2803 (1938).
182a. The Structure of the Insulin Molecule. (With D. M. Wrinch). JACS, **60**, 2247 (1938).
188. Nature of the Cyclol Bond. (With D. M. Wrinch). Nature, **143**, 49 (1939).
189. The Properties and Structure of Protein Films. Proc. Roy. Inst., **30**, 483 (1938).

Digitized by Google Original from UNIVERSITY OF MICHIGAN

191. Properties and Structure of Protein Monolayers. (With V. J. Schaefer). Chem. Rev., **24**, 181 (1939).
192. The Structure of Proteins. Proc. Phys. Soc., London, **51**, 592 (1939).
193. Letter to the Editor on Structure of Proteins. Nature, **143**, 280 (1939).
194. A Note on the Structure of Insulin. (With D. M. Wrinch). Proc. Phys. Soc., London, **51**, 613 (1939).
187. Protein Monolayers. Cold Spring Harbor Symposia on Quantitative Biology, **6**, 171 (1938).
196. Pressure-soluble and Pressure-displaceable Components of Monolayers of Native and Denatured Proteins. (With D. F. Waugh). JACS, **62**, 2771 (1940).

VOLUME 8

Properties of Matter

Part 1 — *Fundamental Properties of Solids and Liquids*

42. The Constitution and Fundamental Properties of Solids and Liquids. JACS, **38**, 2221 (1916).
49. The Constitution and Fundamental Properties of Solids and Liquids. II. Liquids. JACS, **39**, 1848 (1917).

VOLUME 8

Properties of Matter

Part 2 — *Interfacial Phenomena*

43. The Constitution of Liquids with Especial Reference to Surface Tension Phenomena. Met. and Chem. Engrg., **15**, 468 (1916).
48. The Shapes of Group Molecules Forming the Surfaces of Liquids. Proc. NAS, **3**, 251 (1917).
54. The Mechanism of the Surface Phenomena of Flotation. Trans. Faraday Soc., **15**, 62 (1920); G. E. Rev., **24**, 1025 (1921).
146. Surface Chemistry. Nobel Lecture Presented in Stockholm on December 14, 1932. Kungl. Boktryckeriet. P. A. Norstedt and Söner, Stockholm (1933).
153. Surface Chemistry. The Denki-Gakkwai, Iwadare Foundation, Lecture II, Japan (1934).
162. Two-dimensional Gases, Liquids and Solids. Science, **84**, 379 (1936).
176. Surface Electrification due to the Recession of Aqueous Solution from Hydrophobic Surfaces. JACS, **60**, 1190 (1938).
185. Repulsive Forces Between Charged Surfaces in Water and the Cause of the Jones-Ray Effect. Science, **88**, 430 (1938).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

VOLUME 9

SURFACE PHENOMENA

Part 1 — *Evaporation, Condensation, Adsorption*

16. The Vapor Pressure of Metallic Tungsten. Phys. Rev., **2**, 329 (1913).
23. The Vapor Pressure of the Metals Platinum and Molybdenum. (With G. M. J. Mackay). Phys. Rev., **4**, 377 (1914).
112. The Rates of Evaporation and the Vapor Pressures of Tungsten, Molybdenum, Platinum, Nickel, Iron, Copper, and Silver. (With G. M. J. Mackay and H. A. Jones). Phys. Rev., **30**, 201 (1927).
41. The Evaporation, Condensation, and Reflection of Molecules and the Mechanism of Adsorption. Phys. Rev., **8**, 149 (1916).
47. The Condensation and Evaporation of Gas Molecules. Proc. NAS, **3**, 141 (1917).
50. The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum. JACS, **40**, 1361 (1918).
138. Accommodation Coefficient of Hydrogen: a Sensitive Detector of Surface Films. (With K. B. Blodgett). Phys. Rev., **40**, 78 (1932).
140. Vapor Pressures, Evaporation, Condensation, and Adsorption, JACS, **54**, 2798 (1932).
142. A Film Which Adsorbs Atomic H and Does Not Adsorb H_2. (With K. B. Blodgett). JACS, **54**, 3781 (1932).
143. An Extension of the Phase Rule for Adsorption Under Equilibrium and Non-equilibrium Conditions. Jour. Chem. Phys., **1**, 3 (1933).

VOLUME 9

SURFACE PHENOMENA

Part 2 — *Monomolecular Films*

131. Experiments With Oil on Water. Jour. Chem. Education, **8**, 850 (1931).
147. Oil Lenses on Water and the Nature of Monomolecular Expanded Films. Jour Chem. Phys., **1**, 756 (1933).
150. Mechanical Properties of Monomolecular Films. Jour. Franklin Inst., **218**, 143 (1934). Franklin Medal Speech on May 16, 1934.
157. A New Method of Investigating Monomolecular Films. (With K. B. Blodgett). Kolloid-Zeitschrift, **73**, 257 (1935).
158. Composition of Fatty Acid Films on Water Containing Calcium or Barium Salts. (With V. J. Schaefer). JACS, **58**, 284 (1936).
165. Built-up Films of Barium Stearate and Their Optical Properties. (With K. B. Blodgett). Phys. Rev., **51**, 964 (1937).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

167. Optical Measurement of the Thickness of a Film Absorbed from a Solution. (With V. J. Schaefer). JACS, **59**, 1406 (1937).
179a. Overturning and Anchoring of Monolayers. Science, **87**, 493 (1938).
172. The Effect of Dissolved Salts on Insoluble Monolayers. (With V. J. Schaefer). JACS, **59**, 2400 (1937).
181. Effect of X-rays on Surface Potentials of Multilayers. (With F. J. Norton). JACS, **60**, 1513 (1938).
190. Molecular Layers. Pilgrim Trust Lecture. Proc. Roy. Soc., London, **A**, **170**, 1 (1939).
195. Monolayers on Solids. (Seventeenth Faraday Lecture). Jour. Chem. Soc., London, 511 (1940).
113. The Effect of Monomolecular Films on the Evaporation of Ether Solutions. (With D. B. Langmuir). Jour. Phys. Chem., **31**, 1719 (1927).
207. Molecular Films in Chemistry and Biology. Rutgers University Press, 27 (1942).

VOLUME 10

Atmospheric Phenomena

Part 1 — *Aviation, Weather, Cloud Seeding*

51. The Evaporation of Small Spheres. Phys. Rev., **12**, 368 (1918).
77. Radial Flow in Rotating Liquids. (With H. Mott-Smith). [Abstract]. Phys. Rev., **20**, 95 (1922).
135. A Study of Light Signals in Aviation and Navigation. (With W. F. Westendorp). Physics, **1**, 273 (1931).
160. Airplane Tracks in the Surface of Stratus Clouds. (With A. Forbes). Jour. Aeronautical Sci., **3**, 385 (1936).
173. Air Traffic Regulations as Applied to Private Aviation. The Sportsman Pilot, **18**, 8 (1937).
175. Surface Motion of Water Induced by Wind. Science, **87**, 119 (1938).
198. Rates of Evaporation of Water Through Compressed Monolayers on Water. (With V. J. Schaefer). Jour. Franklin Inst., **235**, 119 (1943).
209. The Production of Rain by a Chain Reaction in Cumulus Clouds at Temperatures Above Freezing. Jour. Met., **5**, 175 (1948).
210. The Growth of Particles in Smokes and Clouds and the Production of Snow from Supercooled Clouds. Proc. Amer. Phil. Soc., **92**, 167 (1948).
213. Control of Precipitation from Cumulus Clouds by Various Seeding Techniques. Science, **112**, 35 (1950).
219. A Seven-day Periodicity in Weather in United States during April, 1950. Bull. Amer. Met. Soc., **31**, 386 (1950).
220. Cloud Seeding by Means of Dry Ice, Silver Iodide, and Sodium Chloride. Trans. N.Y. Acad. Sci., **14**, 40 (1951).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

VOLUME 10

Atmospheric Phenomena

Part **2** *— Smoke Filters — Cloud Droplets (Unpublished)*

225. Super-cooled Water Droplets in Rising Currents of Cold Saturated Air. (Report No. RL-223). Parts I and II. October 1943-August 1944. (Re-issued June 1949).
226. Mathematical Investigation of Water Droplet Trajectories. Report No. RL-224. January 1945. (Re-issued June 1949).
227. Mathematical Investigation of Water Droplet Trajectories. Report No. RL-225, December 1944-July 1945. (Re-issued June 1949).
228. Report on Smokes and Filters.

VOLUME 11

Cloud Nucleation

Part **1** *— Nucleation of Clouds with Dry Ice (Unpublished)*

211. Summary of Results Thus Far Obtained in Artificial Nucleation of Clouds. Project Cirrus Report on Meteorological Research (July, 1947).
212. Studies of the Effects Produced by Dry Ice Seeding of Stratus Clouds. Project Cirrus Final Report (December 31, 1948).
214. Progress in Cloud Modification by Project Cirrus. Occasional Report No. 21, Project Cirrus. (April 15, 1950).
215. Cause and Effect Versus Probability in Shower Production. Occasional Report No. 22, Project Cirrus. (July 15, 1950).
216. A Gamma Pattern Seeding of Stratus Clouds, Flight 52, and a Racetrack Pattern Seeding of Stratus Clouds, Flight 53. (With C. A. Woodman). Occasional Report No. 23, Project Cirrus. (June 1, 1950).
217. Results of the Seeding of Cumulus Clouds in New Mexico. Occasional Report No. 24, Project Cirrus. (June 1, 1950).
218. Studies of Tropical Clouds. Occasional Report No. 25, Project Cirrus. (July 1, 1950).

VOLUME 11

Cloud Nucleation

Part **2** *— Nucleation of Clouds with Silver Iodide (Unpublished)*

222. Final Report, Project Cirrus. Part II. Analysis of the Effects of Periodic Seeding of the Atmosphere with Silver Iodide. 340 pages. (May 1953).
229. Widespread Control of Weather by Silver Iodide Seeding. 55-RL-1263. July 1955.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

VOLUME 12

LANGMUIR, THE MAN AND THE SCIENTIST

Part 1 — A Biography

VOLUME 12

LANGMUIR, THE MAN AND THE SCIENTIST

Part 2 — Philosophy of Science

70. Future Developments of Theoretical Chemistry. Chem. and Met. Engrg., **24**, 533 (1921).
115. Atomic Hydrogen as an Aid to Industrial Research. Science, **57**, (February 24, 1928). Printed again in Scientific Monthly, **70**, 3 (1950).
123. Address of Presentation of Priestley Medal Award. Ind. and Engrg. Chem. **21**, 896 (1929).
124. Modern Concepts in Physics and Their Relation to Chemistry. JACS, **51**, 2847 (1929). [President's Address].
126a. Selecting the Chemist-elect. Jour. Chem. Education, **7**, (March, 1930). [Address delivered at dedication of Francis P. Garvan Chair of Chemical Education at Johns Hopkins, October 11, 1929].
149. Science as a Guide in Life. G.E. Rev., **37**, 312 (1934).
155. Mechanical Properties of Matter. Mch. Engrg., **57**, 486 (193 5).
166. Chemical Research. Ind. and Engrg. Chem., **15**, 188 (1937). [Address delivered at the dedication of the new building of Mellon Institute, May 5–9, 1937].
171a. Fundamental Research and its Human Value. G.E. Rev., **40**, 569 (1937).
180. The Speed of the Deer Fly. Science, **87**, 233 (1938).
190a. A chapter "Simple Experiments in Science" on page 3 of book: "Excursions in Science", edited by Neil G. Reynolds and Ellis L. Manning, McGraw-Hill Book Company (1939).
197. Science, Common Sense, and Decency. Science, **97**, 1 (1943). [Retiring President's Address from AAAS].
199. Unforeseeable Results of Research. U.S. Rubber Company Broadcast. (January 21, 1945).
200. Electronics of Tomorrow. N.Y. Herald Tribune Forum. (November 17, 1943).
201. Discussion on Science Legislation. Joint Hearings on Science Bills before Senate Military Affairs and Commerce Committees. (October 1945).
202. Testimony on Atomic Energy Control. Senate Hearings on Atomic Energy. (November 30, 1945).

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

203. World Control of Atomic Energy. Proc. Amer. Phil. Soc., **90**, No. 1 (1946). [Read November 16, 1945 in the Symposium on Atomic Energy and Its Implications].
204. My Trip to Russia. Chem. and Engrg. News, **24**, 759 (1946).
205. Science and Incentives in Russia. Scientific Monthly, **63**, 85 (1946).
206. Faraday Medalist: Response by I. Langmuir to Presentation Address by A. P. M. Fleming. Elec. Engrg., **63**, 463 (1944).
221. Planning for Progress: Two Alternatives. Columbia University Engineering Center News, **1**, 2 (1951). [Talk presented at Columbia University Engineering Center Dinner on November 7, 1951].
223. Saul Dushman — A Human Catalyst. Vacuum, **3**, 112 (1954).
224. Freedom — The Opportunity to Profit from the Unexpected. Res. Lab. Bulletin, Fall 1956.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN